

ORGANIC SYNTHESSES

AN ANNUAL PUBLICATION OF SATISFACTORY
METHODS FOR THE PREPARATION
OF ORGANIC CHEMICALS

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JAMES B. CONANT

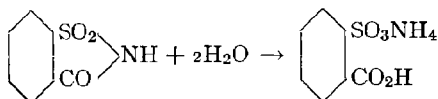
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ORGANIC SYNTHESSES

I

ACID AMMONIUM *o*-SULFOBENZOATE



Submitted by H. T. CLARKE and E. E. DREGER.
Checked by HENRY GILMAN and J. E. KIRBY.

1. Procedure

IN a 12-l. flask fitted with a stirrer and reflux condenser are placed 188 g. (1 mole) of *o*-sulfobenzoyl imide ("saccharin insoluble"), 565 cc. of distilled water and 188 g. of concentrated hydrochloric acid (sp. gr. 1.19). The mixture is boiled over a free flame with continual stirring (Note 1) until all the solid is in solution; this requires two and one-half to three hours. A second quantity of 188 g. of *o*-sulfobenzoyl imide is then added, and the mixture again heated with stirring until a clear solution results, which requires one and one-half to two hours. Heating is then continued for one hour longer, whereupon the solution is poured into a crock and allowed to cool. The crystals which separate are collected on a suction funnel, washed as free from hydrochloric acid as possible (Note 2) with ice-cold distilled water, and dried. The mother liquor and washings are concentrated on a steam bath under reduced pressure until the separation of crystals causes bumping, when the solution is again allowed to crystallize. This procedure is repeated, the final mother liquor being evaporated nearly to dryness. The

main product, together with that from the mother liquors, weighs 410-427 g. (91-95 per cent of the theoretical amount) and is sufficiently pure for conversion into *o*-sulfobenzoic anhydride. In order to obtain a purer product the material may be recrystallized from an equal weight of distilled water; the yield on recrystallizing is about 90 per cent.

2. Notes

1. The mixture tends to foam somewhat during the first few minutes of boiling.

2. If much hydrochloric acid is allowed to remain with the crystals, drying is extremely difficult.

3. Methods of Preparation

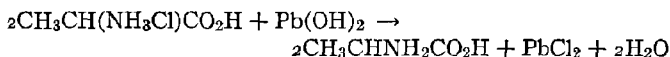
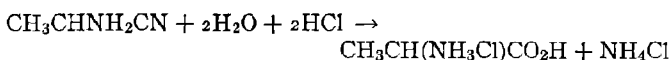
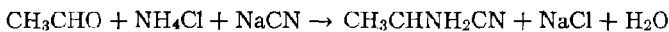
Acid ammonium *o*-sulfobenzoate has been prepared by the hydrolysis of saccharin with concentrated hydrochloric acid.¹ The above method is a modification of that of White and Acree.²

¹ Fahlberg and Barge, Ber. **22**, 755 (1889); Remsen and Linn, Am. Chem. J. **11** 74 (1889).

² White and Acree, J. Am. Chem. Soc. **41**, 1197 (1919).

II

dl-ALANINE



Submitted by E. C. KENDALL and B. F. McKENZIE.

Checked by C. S. MARVEL and W. W. MOYER.

1. Procedure

ONE hundred and thirty-two grams (3 moles) of freshly distilled acetaldehyde (Note 1) is added to 100 cc. of ether in a 2-l. bottle and cooled to 5° in an ice bath (Note 2). One hundred and eighty grams (3.4 moles) of ammonium chloride dissolved in 550 cc. of water is then added, followed by an ice-cold solution of 150 g. (3 moles) of sodium cyanide in 400 cc. of water. The sodium cyanide must be added slowly and with frequent cooling to prevent loss of acetaldehyde by volatilization.

After the sodium cyanide solution is added, the bottle is stoppered securely, placed in a mechanical shaker, and shaken for four hours at room temperature. At the end of this time the solution is transferred to a 3-l. distilling flask and 600 cc. of concentrated hydrochloric acid (sp. gr. 1.19) is added (Note 3).

The solution in the flask is distilled over a free flame until separation of salt prevents further heating. It is then transferred to a large evaporating dish, placed on a steam-bath and evaporated to dryness (Note 4).

The residue remaining in the dish after evaporation is stirred

thoroughly with 800 cc. of 95 per cent alcohol. After filtration the alcohol is distilled on a steam bath and the last traces are removed under vacuum. While still warm the residue is dissolved in 500 cc. of 95 per cent alcohol containing 2 per cent of hydrochloric acid, and cooled. Two hundred cubic centimeters of ether is added, and the solution is filtered. This treatment should remove all but the last traces of sodium chloride and ammonium chloride. The alcohol and ether are removed by distillation and the last of the free hydrochloric acid is removed by distillation under diminished pressure.

The alanine hydrochloride remaining in the flask is dissolved in 1500 cc. of water, and transferred to a metal pail of about 2-l. capacity. Two hundred and twenty grams of yellow lead oxide is added and the mixture is boiled gently for one hour. During the boiling small amounts of water are added at intervals in order to maintain the original volume (Note 5). Upon cooling, the lead chloride crystallizes; it is filtered off and the solution is again boiled one hour with 100 g. of lead oxide. Twenty grams of freshly precipitated lead hydroxide is added slowly and the boiling is continued for ten minutes. Following this the solution is again cooled and filtered (Note 6). The chloride content should now be not more than 50-75 cc. of a normal solution (Note 7).

The solution is again brought to a boil and a calculated amount of silver oxide (Note 7) is added to remove the last of the chlorides. The silver chloride is filtered off and the lead is precipitated with hydrogen sulfide. A light straw-colored solution remains.

The solution is evaporated by boiling to a volume of about 400 cc., and 600 cc. of 95 per cent alcohol is added. When thoroughly cooled, 100-120 g. of alanine is filtered off. This is washed with 200 cc. of alcohol and a pure white product is obtained.

A further crop of 40-50 g. may be obtained by removing the alcohol and water until a volume of about 100 cc. remains, and then adding 250 cc. of alcohol and cooling to 0°. The total yield is 140-160 g. (52-60 per cent of the theoretical amount).

Alanine so prepared is sufficiently pure for most purposes. It may be recrystallized by dissolving in the least amount of water and adding two volumes of alcohol.

2. Notes

1. Acetaldehyde may be conveniently prepared by distilling from paraldehyde in the presence of a trace of sulfuric acid; an efficient fractionating column should be used.

2. A one-half-gallon ginger-ale bottle is convenient for this purpose. The necks of these bottles are small and will hold a wire securely.

3. Caution must be observed during the addition of the hydrochloric acid as considerable hydrogen cyanide is evolved. During the first part of the subsequent distillation it is necessary to prevent fumes from escaping from the receiver into the room.

4. During the evaporation a layer of crystals forms on the surface and must be continually broken. A blast of air blowing over the surface agitates the liquid sufficiently and allows free evaporation.

5. The volume of the solution must be kept large during the treatment with lead oxide as lead chloride will not crystallize from concentrated alanine solutions.

6. If the solution at this point still contains ammonium salts another treatment with 100 g. of lead oxide is necessary.

7. An aliquot portion of the solution is titrated with silver nitrate by the Volhard method. The result of this titration is used in calculating the amount of silver oxide which must be added.

3. Methods of Preparation

dl-Alanine has been prepared by heating ethyl α -chloropropionate with concentrated aqueous ammonia at 100°;¹ by warming α -bromopropionic acid with alcoholic ammonia;² by

¹ H. Kolbe, Ann. **113**, 221 (1860).

² Kekulé, Ann. **130**, 18 (1864).

reducing α -oximinopropionic acid with zinc in hydrochloric acid;³ by reduction of *dl*-serine with hydriodic acid and red phosphorus;⁴ by heating cysteine hydrochloride to 140–150°;⁵ and by heating hydropyruvinureide with aqueous barium hydroxide.⁶

Strecker⁷ first synthesized alanine by the action of hydrocyanic acid on aldehyde ammonia. The present procedure is based on Zelinsky's modification of the Strecker synthesis.⁸

³Gutknecht, Ber. **13**, 1118 (1880).

⁴Fischer and Leuchs, Chem. Zentr. **1902 I**, 762.

⁵Mörner, Z. physiol. Chem. **42**, 360 (1909).

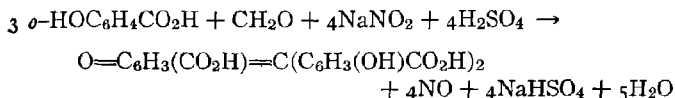
⁶Gabriel, Ann. **348**, 70 (1906).

⁷Strecker, Ann. **75**, 29 (1850).

⁸Zelinsky, Stadnikow, Ber. **41**, 2061 (1908).

III

AMMONIUM SALT OF AURIN TRICARBOXYLIC ACID



Submitted by G. B. HEISIG and W. M. LAUER.

Checked by H. T. CLARKE and ROSS PHILLIPS.

1. Procedure

To 70 cc. of concentrated sulfuric acid (Note 1) in a 1-l. short-neck flask fitted with a mechanical stirrer and immersed in an ice-water bath is added, with vigorous stirring, 10 g. (0.145 moles) of solid sodium nitrite in small portions. The addition is made at such a rate that only a very small amount of nitrogen oxide is evolved. When solution is complete, 20 g. (0.145 moles) of salicylic acid is added in small portions with stirring; about fifteen minutes is required. The mixture is stirred at 20° until all the solid is in solution (Note 2). The mixture should then be light red to brown in color, very viscous, and quite homogeneous. It is surrounded by an ice-salt bath and when the temperature reaches 0°, 5 cc. (0.065 mole) of a 35-40 per cent solution of formaldehyde (formalin) is slowly added with extremely vigorous stirring, at such a rate that the temperature does not rise above 5° (Note 3). The reaction is complete a few minutes after all the formaldehyde has been added. About 100 g. of finely crushed ice is then added, followed by 500 cc. of ice-water; the stirring should be vigorous during the addition (Note 4). The contents of the flask are stirred until the aurin tricarboxylic acid has disintegrated into small pieces. The solid is washed several times by decantation,

using cold water, and finally filtered with suction. It is then dissolved in dilute ammonia (1 volume of concentrated ammonia with 2 volumes of water) while it is still on the filter paper in the suction funnel (Note 5). The filtrate is evaporated to dryness on a steam bath. The resulting glassy, light yellowish-brown ammonium salt, which weighs 19–22 g. (83–96 per cent of the theoretical amount) is sufficiently pure (Note 6) for use as a test for aluminium.

2. Notes

1. The reaction may be carried out somewhat less satisfactorily with the use of 55 cc. of sulfuric acid.

2. If solution is not complete, unchanged salicylic acid will be present in the final product.

3. If the stirring is quite violent, the temperature may be allowed to rise somewhat higher, say to 15–20°, but if the temperature is allowed to rise with only moderate stirring, the yield is lowered owing to the formation of tars.

4. Foaming may occur during the addition of the water but this can be controlled by adding a few drops of ether.

5. The purification of the crude aurin tricarboxylic acid by extracting with hot water¹ is undesirable, for the hot water causes the acid to soften, and results in the formation of large viscous semi-liquid masses which cannot be filtered readily.

6. The method suggested by Caro² for the purification of aurin tricarboxylic acid seems to be unnecessary when the dye is to be used as a test for aluminium. In this method the crude product is dissolved in sodium hydroxide, sodium bisulphite is added until the solution is decolorized, and the addition compound of the free acid is precipitated by adding hydrochloric acid.

3. Methods of Preparation

The preparation of aurin tricarboxylic acid was first described in a patent³ granted to Geigy, in which the foregoing method is

¹ Hammett and Sottery, *J. Am. Chem. Soc.* **47**, 142 (1925).

² Caro, *Ber.* **25**, 939 (1892).

³ Geigy, *Ger. Pat.* 49970, *Frdl.* **2**, 50 (1891).

embodied in one of the examples; another method, involving the action of sodium nitrite upon a warm solution of salicylic acid in a mixture of methyl alcohol and sulfuric acid, is also described in the same patent. It has also been prepared ⁴ by the action of sulfuric acid and nitrite upon a mixture of salicylic acid and 3,3'-dicarboxy-4,4'-dihydroxydiphenylmethane ("ethylene disalicylic acid"), which is formed from salicylic acid with formaldehyde in presence of hydrochloric acid.

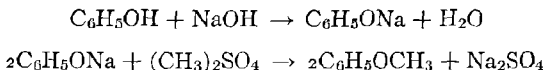
Aurin tricarboxylic acid is of interest as a reagent for detecting aluminium.⁵

⁴ Caro, Ber. **25**, 939 (1892).

⁵ Hammett and Sottery, J. Am. Chem. Soc. **47**, 142 (1925).

IV

ANISOLE



Submitted by G. S. HERS and F. D. HAGER.

Checked by HENRY GILMAN, S. A. HARRIS, and G. WRIGHT.

1. Procedure

In a 5-l. two-neck round-bottom flask fitted with an efficient stirrer, separatory funnel, and reflux condenser is placed a mixture of 235 g. (2.5 moles) of phenol and 100 g. (2.5 moles) of sodium hydroxide (Note 1) in 1 l. of water. The mixture is cooled, with stirring, in an ice-salt bath to below 10°. There is then added through the separatory funnel 315 g. (2.5 moles) of dimethyl sulfate (Note 2). This addition requires about one hour and the cooling bath is not removed until the addition is complete. The mixture is then heated on a water bath for half an hour. At the end of this time there is added through the separatory funnel a mixture of 235 g. (2.5 moles) of phenol and 100 g. (2.5 moles) of sodium hydroxide in 1 l. of water. This addition requires about fifteen minutes. The mixture is then refluxed vigorously over a free flame for fifteen hours (Note 3).

The mixture is cooled and the anisole layer is separated. The aqueous portion is extracted with about 200 cc. of benzene (Note 4). The combined anisole-benzene portion is washed once with water, dried over calcium chloride and distilled from a modified Claisen flask (Org. Syn. 1, 40). The portion boiling at 100–153° is refractionated. The main fraction distills at 153–154°/748 mm. The yield is 388–405 g. (72–75 per cent of the theoretical amount) (Notes 5 and 6).

2. Notes

1. The sodium hydroxide was a high quality technical grade.
2. Dimethyl sulfate is toxic, but with due care to avoid spattering of the liquid and inhaling of the vapor the operation may be carried out without the use of a hood. A good technical grade of dimethyl sulfate was used.
3. When the period of refluxing is shorter, the yield is materially decreased. The first methyl group reacts easily but the second only with considerable difficulty. A longer period of refluxing does not give much larger yields. As the sodium sulfate concentration increases, the dimethyl sulfate hydrolyzes less readily.
4. A separate fractional distillation of this benzene extract yields 9-18 g. of anisole. The major part of the anisole contained in the aqueous layer may be recovered by steam distillation instead of a benzene extraction. Neither method of recovery is wholly satisfactory.
5. When only one-half the amount of phenol is used, the yield is 85-92 per cent but with fairly inexpensive phenol it is more profitable to operate in such a manner that both methyl groups of the dimethyl sulfate are used.
6. Other methyl ethers may be prepared by a similar procedure. β -Naphthyl methyl ether is obtained in a 65-73 per cent yield by adding the dimethyl sulfate over a period of thirty minutes to equivalent quantities of β -naphthol and sodium hydroxide kept cool by an ice-water bath, then heating for one hour at 75-78°, and, finally, crystallizing from benzene to obtain the pure methyl ether which melts at 71°.

3. Methods of Preparation

Anisole has been prepared by a variety of other methods, the most important being: from sodium or potassium phenolate and methyl iodide;¹ from sodium phenolate and methyl chloride;²

¹ Cahours, Ann. 78, 225 (1851); Segaller, J. Chem. Soc. 105, 112 (1914).

² Vincent, Bull. soc. chim. (2) 40, 106 (1883).

from potassium phenolate and sodium methyl sulfonate;³ from benzene diazonium nitrate and methyl alcohol;⁴ sodium benzene sulfonate and sodium methylate;⁵ phenol and methyl alcohol in the presence of thorium oxide;⁶ from phenol, methyl alcohol and β -naphthalene sulfonic acid⁷ or potassium hydrogen sulfate;⁸ and by the methylation of phenol with dimethyl sulfate or methyl ethyl sulfate.⁹

³ Nollau and Daniels, J. Am. Chem. Soc. **36**, 1890 (1914).

⁴ Beeson, Amer. Chem. J. **16**, 235 (1894).

⁵ Moureu, Bull. soc. chim. (3) **19**, 399 (1898).

⁶ Sabatier and Mailhe, Compt. rend. **151**, 359 (1910).

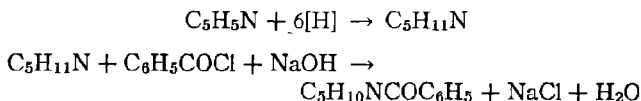
⁷ Krafft and Roos, Ger. pat. 76, 574, Frdl. IV, 17.

⁸ Actiengesellschaft für anilinfabrikation in Berlin, Ger. pat. 23, 775, Frdl. I, 43.

⁹ Thayer, J. Am. Chem. Soc. **46**, 1046 (1924).

V

BENZOYL PIPERIDINE



Submitted by C. S. MARVEL and W. A. LAZIER.

Checked by J. B. CONANT, J. S. ANDREWS, and C. O. TONGBURG.

1. Procedure

In a 5-l. two-neck round-bottom flask, fitted with an efficient reflux condenser (Note 1), is placed a mixture of 130 g. (1.64 moles) of dry pyridine (Note 2) and 3 l. of absolute alcohol. During the course of forty to fifty minutes 450 g. (19.6 moles) of sodium is added gradually. The sodium is added in as large pieces as can be inserted through the second opening in the flask. One and one-half liters of absolute alcohol is now added and the mixture heated over an oil bath for two to three hours until the sodium disappears. It is desirable not to allow the reaction mixture to cool (Note 3) at this point but to separate the piperidine immediately. The condenser is set for distillation and a separatory funnel is inserted through the stopper in the second opening of the flask. The alcohol is then distilled using an oil bath (Note 4). The addition of a piece of zinc facilitates an even distillation. During this procedure, water to the amount of 1700-1800 cc. is added to the reaction mixture through the separatory funnel, slowly at first and later as rapidly as possible. At the beginning, this addition must be very cautious as the heat evolved causes a very rapid distillation of alcohol. After about 200 cc. of water has been added the mixture begins to solidify and remains semi-solid until most of the water has been added.

The distillation is continued until practically all the alcohol has distilled (three to four hours). At the end of this time there remains in the distilling flask about 1500 cc. of residue, which is discarded. The distillate is about 5 l. in volume. To this is added 200 cc. of concentrated hydrochloric acid (sp. gr. 1.19) and the mixture is then returned to the distilling flask. The alcohol is removed by distillation on a steam bath until the residual volume in the flask amounts to about 600-800 cc.; this requires two to three hours. The residue is then transferred to a 2-l. round-bottom flask fitted with a mechanical stirrer and separatory funnel. The mixture is treated with stirring with a solution of 186 g. of technical sodium hydroxide or 170 g. (4.25 moles) of c. p. sodium hydroxide in about 300 cc. of water. With continuous stirring 235 g. (1.67 moles) of benzoyl chloride is now added during the course of an hour, keeping the temperature down by cooling with running water. After the addition, the reaction mixture is cooled, the amide separated (Note 5), washed with a little water (Note 6) and distilled (Note 7) under reduced pressure. The product boils at 180-184°/20 mm., 191-194°/27 mm., 240-244°/130 mm., and weighs 240-250 g. (77-81 per cent of the theoretical amount).

Benzoyl piperidine thus obtained is a straw-colored viscous liquid. Upon long standing or seeding with crystalline benzoyl piperidine, the compound crystallizes in long, colorless needles which melt at 44°. The literature reports 48° as the melting point of the pure material.

Using 180 g. of pyridine in place of the 130 g. suggested, and a corresponding increase in the other chemicals except the sodium and alcohol, a yield of 300-326 g. of benzoyl piperidine is obtained. This is a smaller percentage yield (70-75 per cent of the theoretical amount) but the actual yield more than repays for the excess of pyridine used (see also Note 8).

2. Notes

1. A reflux condenser ~~30 cm. long~~ with inner tube 2 cm. in diameter is recommended. If a smaller condenser is employed,

the reaction cannot be run as rapidly as is desirable to give the best results. If the reaction is not run rapidly sodium ethylate separates in the flask.

2. Unless the purity of the pyridine is known, it should be dried with solid sodium hydroxide and distilled before use. For this work a fraction boiling at $112-117^{\circ}$ was used.

3. If the alcohol solution is allowed to cool before the addition of the water, it solidifies and is remelted only with difficulty. If it is desired to suspend the process, the water should be added first and then the solution will not solidify.

4. In distilling the piperidine from the strong alkaline solution, the flask must be suspended in the oil bath. Direct heating raises the temperature of flask to such a point that the alkali rapidly eats through it.

5. A troublesome emulsion sometimes results after benzoylation. This may be broken up usually by the addition of more strong sodium hydroxide solution. In case an emulsion is formed which cannot be broken it is possible to extract the product with benzene.

6. Any sodium hydroxide carried into the distilling flask causes decomposition of the benzoyl piperidine during distillation and consequently a considerably lower yield results. For this reason it is well to wash the product carefully in the separatory funnel with a little water after the alkaline solution has been drawn off.

7. Benzoyl piperidine is much given to superheating, making distillation difficult.

8. If piperidine is available, benzoyl piperidine for use in the preparation of pentamethylene bromide (p. 70) may be prepared by direct benzoylation. A mixture of 105 g. of sodium hydroxide (2.6 moles), 170 g. of piperidine (2.0 moles) (b. p. $104-108^{\circ}$) and 800 cc. of water are treated with 280 g. (2 moles) of benzoyl chloride using the apparatus and procedure described above; the temperature is kept at $35-40^{\circ}$. The oily product is separated after dilution with 250 cc. of benzene if necessary (Note 5), dried with a small quantity of potassium carbonate and distilled. The portion boiling at $172-174^{\circ}/12$ mm. weighs 330-345 g. (87-91 per cent of the theoretical amount). The first few

cubic centimeters of the distillate may be colored by a reddish impurity in which case a fore-run is collected separately.

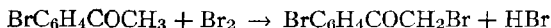
3. Methods of Preparation

Benzoyl piperidine has been prepared only by the action of benzoyl chloride on piperidine in the presence of alkalies.¹

¹ Cahours, *Ann. chim. phys.* (3) **38**, 87 (1853); Schotten, *Ber.* **17**, 2545 (1884); **21**, 2238 (1888).

VI

p-BROMOPHENACYL BROMIDE



Submitted by W. D. LANGLEY

Checked by H. T. CLARKE and P. W. BOUTWELL.

1. Procedure

IN a 500-cc. flask are placed 50 g. (0.25 mole) of *p*-bromoacetophenone (Org. Syn. 5, 17) and 100 cc. of glacial acetic acid. To the resulting solution is very slowly added 40 g. (0.25 mole) of bromine, keeping the temperature below 20°. The mixture is vigorously shaken by hand during the addition. *p*-Bromophenacyl bromide begins to separate as needles when about one-half of the bromine has been added. The addition requires about thirty minutes.

When all the bromine has been added, the flask is cooled in ice-water and the product filtered with suction. The crude crystals are washed with 50 per cent ethyl alcohol until colorless (about 100 cc. is required). The material so obtained, when air-dried, melts at 106–108° and weighs 55–60 g. It is recrystallized from 400 cc. of 95 per cent ethyl alcohol, from which it separates as colorless needles melting at 108–109°. The yield (Note 1) is 48–50 g. (69–72 per cent of the theoretical amount).

2. Notes

1. A further quantity of less pure material may be obtained from the mother liquor from the recrystallization. If the acetic acid mother liquor is treated with water until turbid and then chilled, 4–5 g. of yellow crystals may be obtained. The material recovered from both liquors (6–8 g. in all) cannot be obtained

in a perfectly colorless condition but the melting point is correct after recrystallization from alcohol.

2. Judefind and Reid¹ have shown that many acids may be identified by conversion into their *p*-bromophenacyl esters by the action of *p*-bromophenacyl bromide on the sodium salts.

3. Methods of Preparation

p-Bromophenacyl bromide has been prepared by the interaction of bromobenzene and bromoacetyl chloride in the presence of aluminum chloride² and by the bromination of *p*-bromoacetophenone.^{1, 3}

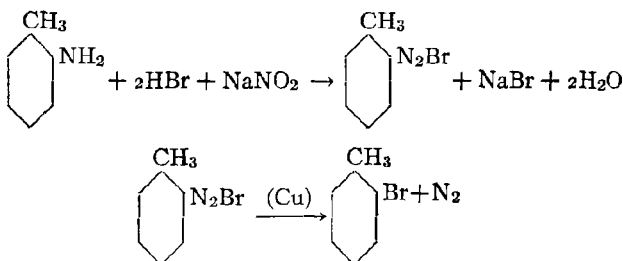
¹ Judefind and Reid, *J. Am. Chem. Soc.* **42**, 1045 (1920).

² Collet, *Compt. rend.* **125**, 717 (1897).

³ Collet, *Bull. soc. chim.* (3) **21**, 67 (1899).

VII

o-BROMOTOLUENE



Submitted by L. A. BIGELOW.

Checked by C. S. MARVEL and S. V. PUNTAMBEKER.

1. Procedure

A SOLUTION of 162 g. (1.5 moles) of commercial *o*-toluidine in 880 cc. (6 moles) of 40 per cent commercial hydrobromic acid (Note 1) in a 3-l. flask is cooled to 10° and diazotized with 116 g. (1.7 moles) of coarsely powdered commercial sodium nitrite, added about 10 g. at a time. After each addition the flask is stoppered and shaken until all the red fumes are absorbed. The temperature must be kept below 10°. When diazotization is complete, 5 g. of copper powder (Note 2) is added, the flask is attached to a reflux condenser and heated very cautiously. As soon as the first sign of reaction is observed, the flask is cooled with ice. Nitrogen is evolved vigorously. When the reaction subsides, the mixture is heated half an hour on the steam bath. Then 1 l. of water is added and the mixture is distilled with steam until about 1.5 l. has passed over. The distillate is made alkaline with about 10 g. of powdered sodium hydroxide and the red bottom layer of crude *o*-bromotoluene separated (Note 3).

This weighs about 140 g. It is washed with concentrated sulfuric acid, which removes almost all the color, and then twice with water. It is dried over a little calcium chloride, filtered and distilled twice from a modified Claisen flask (Org. Syn. 1, 40). The yield of pure product boiling at 178–181° is 110–120 g. (42–47 per cent of the theoretical amount).

2. Notes

1. If 48 per cent (constant boiling) hydrobromic acid is used the diazotization is very difficult to control. The reaction becomes very vigorous and forces out the stopper.

2. Either reduced copper or fine copper filings may be used.

3. This gives as good results as when the o-bromotoluene is extracted from the alkaline mixture with ether.

3. Methods of Preparation

o-Bromotoluene has been obtained by the bromination of toluene;¹ by the bromination of potassium *p*-toluene sulfonate and subsequent hydrolysis;² and by diazotization of o-toluidine under different conditions.³

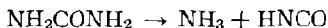
¹ Jannasch and Hübner, Ann. 170, 117 (1873).

² Miller, J. Chem. Soc. 61, 1027 (1892).

³ Wroblevsky, Ann. 168, 171 (1873); Koerner, Gazz. chim. ital. 4, 305 (1874); Jackson, Am. Chem. J. 1, 100 (1879); Feitler, Z. physik. Chem. 4, 72 (1889).

VIII

n-BUTYL CARBAMATE



Submitted by TENNEY L. DAVIS and STANLEY C. LANE.
Checked by H. T. CLARKE and L. G. S. BROOKER.

1. Procedure

IN a 2-l. round-bottom flask fitted with a reflux condenser is placed 1200 cc. (970 g., 13.1 moles) of *n*-butyl alcohol. This is warmed and 180 g. (3 moles) of urea is added to the warm liquid in small portions, with shaking, while the temperature rises, care must be taken that the urea goes into solution without melting and does not form a layer of molten urea beneath the solution (Note 1). The last portions of the urea are finally dissolved by boiling the liquid. The solution is then refluxed for thirty hours (Note 2), during which time ammonia escapes from the top of the condenser (Note 3). The reflux condenser is then removed and the liquid is distilled through an efficient column until the temperature of the liquid reaches 150°. The distillate consists of butyl alcohol containing ammonia and may be used directly in another run. The material which remains in the flask solidifies on cooling. It is boiled with 1 l. of ligroin (b. p. 60–90°) (Note 4), filtered, and the undissolved solid again boiled with two 100-cc. portions of ligroin, filtered and finally washed on the filter with 100 cc. more of warm ligroin. The white gritty material which remains undissolved is practically pure cyanuric acid (Note 5). The yield of cyanuric acid is 12–18 g. (9–14 per cent of the theoretical amount).

The combined ligroin filtrates and washings are distilled under atmospheric pressure, using a column, until the temperature of the liquid reaches 150°. The residue is then distilled under reduced pressure and the fraction boiling at 108–109°/14 mm. (Note 6) is collected. The product is pure and melts at 53–54°. The yield is 263–266 g. (75–76 per cent of the theoretical amount.)

2. Notes

1. If molten urea settles to the bottom near the source of heat, it will cause the liquid to bump and will decompose to produce cyanuric acid to the detriment of the yield of butyl carbamate.

2. If thirty hours of continuous heating is impracticable, care must be taken, on resuming the heating, that the urea goes into solution without melting.

3. A small amount of ammonium carbamate collects in the condenser during the reaction and may cause clogging. This should be removed from time to time by pushing it down by means of a glass tube which fits snugly into the condenser. The gases evolved when the solid falls into the hot liquid are carried off through the tube.

4. "Aviation" gasoline (86° Baumé) may also be employed if it is first distilled and the fraction boiling above 120° rejected.

5. The extraction with ligroin may be completed satisfactorily by means of the apparatus described in *Org. Syn.* 2, 48 (1922). Butyl allophanate is not soluble in ligroin and, if present, would remain with the cyanuric acid. However, when the material which is insoluble in ligroin is washed with hot acetone the washings yield no appreciable residue on evaporation. This is evidence that butyl allophanate and urea are not present in the cyanuric acid.

6. n-Butyl carbamate boils under atmospheric pressure at 203–204° with some decomposition. The products of the decomposition are butyl alcohol and cyanuric acid.

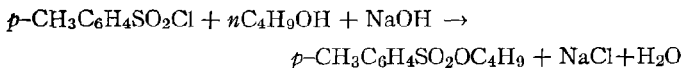
3. Methods of Preparation

No reference to the preparation of *n*-butyl carbamate is to be found in the literature. The above process is adapted from that of Cahours,¹ who prepared *n*-propyl carbamate by heating propyl alcohol with urea. *n*-Butyl carbamate has also been prepared by one of the editors by the action of *n*-butyl chloroformate upon ammonia.

¹ Cahours, Compt. rend. **76**, 1387 (1873).

IX

n-BUTYL *p*-TOLUENESULFONATE



Submitted by A. T. ROOS, HENRY GILMAN, and N. J. BEABER.

Checked by H. T. CLARKE and G. S. BABCOCK.

1. Procedure

In a 2-l., three-neck flask, fitted with a mechanical stirrer, a thermometer, and a 250-cc. separatory funnel, are placed 148 g. (2 moles) of *n*-butyl alcohol and 210 g. (1.1 moles) of pure *p*-toluenesulfochloride (Note 1). From the separatory funnel 320 cc. (1.6 moles) of 5 N sodium hydroxide is run in at a rate that does not cause the temperature of the reaction mixture to exceed 15° (Note 2); the addition requires three to four hours.

Another portion of 210 g. (1.1 moles) of *p*-toluenesulfochloride is added and then 320 cc. of 5 N sodium hydroxide solution is slowly introduced, again keeping the temperature below 15°. Stirring is continued for four hours longer, and the oily layer is separated from the water layer and any unchanged *p*-toluenesulfochloride. Enough petroleum ether (b. p. 60–70°) or benzene is added to the oil to cause it to float on water, the solution is washed thoroughly with 50 cc. of 10 per cent sodium hydroxide, and dried by standing overnight over 20 g. of anhydrous potassium carbonate. The solution is filtered, and the solvent is distilled. This is conveniently accomplished by adding the solution from a separatory funnel to a 500-cc. Claisen flask heated on a steam bath. The oily ester is then distilled in a vacuum (Note 3) and, after a forerun that comes over up to 170°/10 mm., the pure ester distils at 170–171°/10 mm. The yield is 250–270 g. (50–54 per cent of the theoretical amount).

2. Notes

1. Technical *p*-toluenesulfochloride is dissolved in benzene, washed with 5 per cent sodium hydroxide, dried by shaking with a small amount of potassium carbonate, and then distilled in a vacuum. If the vacuum distillation must be interrupted, it is recommended that the liquid be allowed to cool before breaking the vacuum; otherwise, when distillation is resumed later, considerable decomposition takes place.

2. The cooling may be effected conveniently by immersing the flask in a water bath containing a small amount of ice, or by cold running water. If the bath is cooled to 0°, the time required for the completion of the reaction is appreciably longer.

3. It is best to distil the ester under a very high vacuum. Appreciable decomposition takes place even at 1p-mm. pressure, and the distilled ester becomes quite dark after standing a week. To avoid superheating and consequent decomposition, it is recommended that the ester be distilled in small lots (from 250-cc. Claisen flasks when large runs are made). A sample of 100 g. distilled at 132–133°/3 mm. remained water-white after standing for two months.

4. Methyl *p*-toluenesulfonate may be prepared in a somewhat similar manner with good yields. One kilo of methyl alcohol (90–95 per cent) is placed in a round-bottom flask, placed in an ice-salt bath. One kilo of powdered pure *p*-toluenesulfochloride (crude material may be used but the yield of product drops to about 75 per cent) is added with mechanical stirring. From a separatory funnel 840 g. of 25 per cent sodium hydroxide solution is added drop by drop. The temperature must be held at about 23–27° for the best results. When all this alkaline solution is added the reaction mixture is tested with litmus; if not alkaline, more alkali is added until the neutral point is reached. Upon standing several hours the ester sinks and the alcohol forms the top layer. The alcohol may be siphoned off and used in subsequent experiments, the methyl *p*-toluenesulfonate is washed with water to remove a little salt and then with 5 per cent hydrochloric acid to dissolve the iron. Finally it is

washed with 5 per cent sodium carbonate and water. The ester is then distilled and boils at $161^{\circ}/10$ mm. (m. p. $27-28^{\circ}$). The yield is 90 per cent.

The spent alcohol is distilled from a steam bath, and alcohol of 84-91 per cent purity is obtained which is suitable for subsequent runs.

3. Methods of Preparation

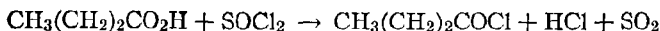
Other alkyl esters of arylsulfonic acids have been prepared by this general method.¹ The *n*-butyl ester has been prepared by treating an ethereal solution of *p*-toluenesulfochloride and butyl alcohol with powdered potassium hydroxide,² and by refluxing the acid chloride with a 10 per cent excess of alcohol.²

¹ Kraft and Roos, Ber. 25, 2255 (1892); Foldi, Ber. 53, 1836 (1920); Izmailski and Razorenov, J. Russ. Phys. Chem. Soc. 52, 359 (1920), [C. A. 18, 1481 (1924)].

² Gilman and Beaber, J. Am. Chem. Soc. 47, 518 (1925).

X

n-BUTYRYL CHLORIDE



Submitted by B. HELFERICH and W. SCHAEFER.

Checked by HENRY GILMAN and S. A. HARRIS.

1. Procedure

IN a 125-cc. distilling flask, provided with a water-cooled side arm to act as reflux condenser (Note 1), is placed 56 g. (0.47 mole) of thionyl chloride (Note 2). This is heated on a water-bath and to it is added during the course of an hour 35.2 g. (0.4 mole) of *n*-butyric acid (Note 3) by means of a separatory funnel attached to the neck of the flask. The evolved gases are absorbed in water.

When all the acid has been added, the mixture is heated for one-half hour on the water bath and then distilled directly from an oil bath into a second distilling flask. The crude acid chloride thus obtained boils between 70–110°; it is purified by distillation through a column and boils almost entirely at 100–101°, only a few drops of forerun being obtained. The yield is 36 g. (85 per cent of the theoretical amount).

2. Notes

1. If a Claisen distilling flask is used for the preparation of the acid chloride the side-arm is plugged; the short neck holds the reflux condenser, and the long neck the separatory funnel.

2. The yield is influenced by the purity of the thionyl chloride; the results reported above were obtained with a pure product which boiled over a two-degree range.

3. The presence of traces of water in the butyric acid is of no disadvantage if a correspondingly larger quantity (1 mole for 1 mole of water) of thionyl chloride is used.

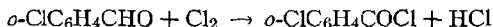
3. Methods of Preparation

n-Butyryl chloride has been prepared from *n*-butyric acid and phosphorus trichloride.¹

¹ Burcker, Ann. chim. phys. (5) **26**, 468 (1882).

XI

o-CHLOROBENZOYL CHLORIDE



Submitted by H. T. CLARKE and E. R. TAYLOR.

Checked by F. C. WHITMORE and H. H. ROWLEY.

1. Procedure

In a 3-l. round-bottom flask, fitted with a thermometer, a reflux condenser, and an inlet tube extending nearly to the bottom, is placed 141 g. (1 mole) of freshly distilled *o*-chlorobenzaldehyde (Note 1). To the upper end of the condenser is attached a tube leading to a flask containing water for the absorption of hydrogen chloride. The reaction vessel and absorption flask are accurately weighed, and a current of chlorine, dried by sulfuric acid, is passed into the aldehyde, the temperature of which is maintained at 140–160°. The rate of the current of gas is so regulated that little or no chlorine escapes. The reaction and absorption flasks are removed and weighed about every three hours. After about fifteen hours (Note 2) the absorption of chlorine at 160° practically ceases. The total increase in weight (Note 3) amounts to 26–29 g. (75–84 per cent of the theoretical amount). The reaction product is distilled under reduced pressure, when the pure *o*-chlorobenzoyl chloride passes over at 93–95°/10 mm. or 137–139°/60 mm., leaving a small quantity of high boiling residue which appears to consist mainly of an intermediate compound (Note 2). The yield is 122–126 g. (70–72 per cent of the theoretical amount) (Note 4).

2. Notes

1. Technical *o*-chlorobenzaldehyde of high purity is available. After one distillation under reduced pressure (b. p. 84°/10 mm., 125°/85 mm.), it melts at 7–10°.

2. If the mixture be kept at 125–140°, the reaction requires about thirty hours for completion. When about one-half of the necessary amount of chlorine has been added, the reaction mixture, if allowed to cool, sets to a colorless mass of an addition compound of the aldehyde and acid chloride; this on further chlorination yields *o*-chlorobenzoyl chloride.

3. The increase in weight is distributed between the reaction flask and hydrochloric acid absorption flask in the ratio of about 45 : 55.

4. The use of large quantities and vigorous mechanical stirring gives much better yields. Thus, a run of 2665 g. (18.9 moles) of the aldehyde gave a yield of 2700 g. (81 per cent of the theoretical amount).

3. Methods of Preparation

The only practical methods for the preparation of *o*-chlorobenzoyl chloride to be found in the literature consist in the treatment of *o*-chlorobenzoic acid with phosphorus pentachloride¹ or thionyl chloride.² It has, however, also been formed by distilling salicylic acid or its sodium salt with phosphorus pentachloride,³ and by heating the dichloride of *o*-sulfobenzoic acid.⁴

¹ Emmerling, Ber. 8, 883 (1875).

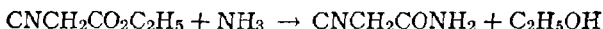
² H. Meyer, Monatsh. 22, 427 (1901); Frankland, Carter and Adams, J. Chem. Soc. 101, 2476 (1912).

³ Chiozza, Ann. 83, 317 (1852); Kolbe and Lautemann, Ann. 115, 183 (1860); Reichenbach and Beilstein, Ann. 132, 311 (1864).

⁴ Remsen and Kohler, Amer. Chem. J. 17, 332 (1895); Fritsch, Ber. 29, 2299 (1896); List and Stein, Ber. 31, 1653 (1898).

XII

CYANOACETAMIDE



Submitted by B. B. CORSON, R. W. SCOTT, and C. E. VOSE.

Checked by C. S. MARVEL and L. H. BOCK.

1. Procedure

Four hundred grams (3.5 moles) of ethyl cyanoacetate (Org. Syn. 3, 53; 8, 74) is poured into 300 cc. (4.5 moles) of concentrated aqueous ammonia (sp. gr. 0.90) (Note 1) contained in a 1-l. wide-mouth Erlenmeyer flask. The mixture, which is cloudy at first, is shaken; it then warms up a little and becomes clear in about three minutes. The flask is allowed to stand one hour in an ice-salt mixture. The product is then filtered by suction (Note 2) and the solid washed with two 50-cc. portions of ice-cold ethyl alcohol (Note 3). After drying in the air, the slightly yellowish, crystalline amide weighs 205-225 g. A snow-white product is easily obtained by crystallizing from hot alcohol (Notes 4 and 5). For this purpose 200 g. of amide is dissolved in 350 cc. (Note 6) of hot alcohol and the solution cooled; pure amide is deposited with practically no loss.

An additional yield of amide is obtained by evaporating (Note 7) the original mother liquor to dryness in a vacuum while heating the flask in a boiling water bath. The damp, brownish residue in the flask is dissolved in 100 cc. of hot alcohol. The hot solution is shaken a few minutes with decolorizing charcoal, filtered by suction while still hot, and then cooled in ice. Forty-six to fifty-eight grams of yellowish amide is deposited. One more crystallization with charcoal yields 44-56 g. of pure product.

The total yield is 255-261 g. (86-88 per cent of the theoretical amount). The product melts at 119-120°.

2. Notes

1. Gaseous ammonia was tried with poor success, the ammonia being passed into the ester (both cold and at room temperature) and also into an alcoholic solution of the ester.

2. The product must be filtered rapidly while the mother liquor is cold because of the solubility of the amide.

3. Cyanoacetamide may be washed with ice water but cold alcohol is preferable because of its lower solubility in the latter.

4. The solubility of cyanoacetamide in 100 cc. of 95 per cent alcohol follows:

1.3 g. at 0°	9.5 g. at 52°
1.7 g. at 12°	14.0 g. at 62°
3.1 g. at 26°	16.3 g. at 66°
5.0 g. at 38°	18.7 g. at 69°
7.0 g. at 44°	21.5 g. at 71°

5. The alcoholic mother liquor from the crystallization usually contains a small amount of malonamide which melts at 170-171°.

6. If the treatment with decolorizing charcoal is necessary, about 450 cc. of alcohol should be used in order to avoid crystallization during the filtration.

7. A few cubic centimeters of an oil, presumably unchanged ethyl cyanoacetate, comes over with the water.

8. This work was done with the aid of a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

3. Methods of Preparation

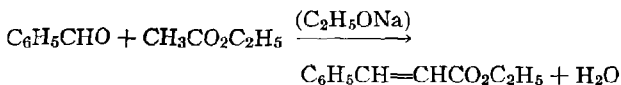
Cyanoacetamide has been prepared only by the action of aqueous¹ or alcoholic² ammonia on cyanoacetic ester.

¹ Van't Hoff, *Ber.* **7**, 1383 (1874); Henry, *Bull. soc. chim.* (2) **48**, 656 (1887); Hesse, *Amer. Chem. J.* **18**, 724 (1896); Thole and Thorpe, *J. Chem. Soc.* **99**, 429 (1911).

² Hesse, *Am. Chem. J.* **18**, 724 (1896); Ott and Löpmann, *Ber.* **55**, 1258 (1922).

XIII

ETHYL CINNAMATE



Submitted by C. S. MARVEL and W. B. KING.

Checked by HENRY GILMAN, R. E. FOTHERGILL, and R. E. BROWN.

1. Preparation

IN a 2-l. two-neck flask fitted with a short reflux condenser and mechanical stirrer (Note 1) are placed 400 cc. of dry xylene (Note 2) and 29 g. (1.26 moles) of clean sodium (Note 3) cut in small pieces. The flask is surrounded by an oil-bath and heated until the sodium has melted. At this point the stirrer is started and the sodium is broken up into very small particles (Note 4). The oil-bath is removed but stirring is continued until the sodium has solidified as very fine particles. The xylene is then poured off, and to the sodium is added 455 cc. (4.7 moles) of absolute ethyl acetate (Note 5) containing 3-4 cc. of absolute ethyl alcohol (Note 6). The flask is quickly cooled to 0° and 106 g. (1 mole) of pure benzaldehyde (Note 7) is added slowly from a separatory funnel while the mixture is stirred. The temperature is held between 0° and 5° (Note 8). The reaction starts as soon as the benzaldehyde is added, as is shown by the production of a reddish substance on the particles of the sodium. About one and a half to two hours are required for this addition. The stirring is continued until practically all of the sodium has reacted (one hour after all the aldehyde has been added). When most of the sodium (Note 9) has disappeared, 90-95 cc. of glacial acetic acid is added and the mixture is carefully diluted with

water. The ester layer is separated, the water layer is extracted with about 25–50 cc. of ethyl acetate, and the combined ester portions are washed with 300 cc. of 6 N hydrochloric acid and then dried with sodium sulfate. The ethyl acetate is distilled from a water-bath and the remaining liquid is transferred to a Claisen flask and distilled from an oil-bath under reduced pressure. A small fraction comes over below $128^{\circ}/6$ mm. and is discarded. The ethyl cinnamate (Note 10) boils at $128\text{--}133^{\circ}/6$ mm.; $168\text{--}173^{\circ}/46$ mm. The yield is 120–130 g. (68–74 per cent of the theoretical amount).

2. Notes

1. The stirrer must be very efficient in order to powder the sodium without splashing it onto the walls of the flask above the solvent.

2. The use of sodium powdered under xylene allows the reaction to be carried out much more rapidly than is the case if the sodium is cut into small pieces with a knife. Toluene may be used in place of xylene. The sodium should be as free as possible from oxide.

3. To obtain the maximum yield it is necessary to use slightly more than one equivalent of sodium. When exactly one equivalent is used the yield is about 60 per cent of the theoretical amount.

4. The powdered sodium may also be prepared by melting the sodium under hot xylene and shaking in a tightly stoppered flask wrapped in a heavy cloth.

5. The grade of ethyl acetate used in the preparation is very important. The absolute ethyl acetate (99.7 per cent) sold by the U. S. Industrial Alcohol Company is very satisfactory. If this grade is not available the ordinary ester may be purified by washing first with sodium carbonate solution, then with saturated calcium chloride solution and finally drying over anhydrous potassium carbonate.

6. A small amount of absolute alcohol is needed to start the reaction. When no alcohol is added the yields are consistently

55-60 per cent of the theoretical amount. When too much alcohol (10-15 cc.) is added the yields drop again.

7. Technical benzaldehyde is washed with sodium carbonate and distilled in a vacuum before use. The material used in checking these directions boiled over a 3° range.

8. The temperature should never be allowed to go above 10° and the best yields of pure product are obtained when the temperature is kept within the limits mentioned in the procedure.

9. Usually during the reaction a certain amount of sodium is thrown on the upper part of the flask out of the reaction mixture and forms a cake. In decomposing the mixture with glacial acetic acid and water care must be taken that this sodium does not react violently and thus cause a fire.

10. During the distillation of the ester a reddish semi-solid mass sometimes appears in the flask. This mass melts down if the oil bath is heated to 220-230° and the distillation continues smoothly.

3. Methods of Preparation

Ethyl cinnamate occurs in small amounts in storax.¹ It has been prepared by the action of ethyl alcohol on cinnamic acid in the presence of dry hydrochloric or sulfuric acid;² by the distillation of the copper salt of the monoethyl ester of benzylidene oxalacetic acid³ and by the condensation of ethyl acetate and benzaldehyde in the presence of sodium.⁴ The method described in the procedure is a slight modification of the one originally described by Claisen.⁵

¹ Miller, Ann. 188, 203 (1877).

² Kopp, Ann. 95, 318 (1855); Weger, Ann. 221, 75 (1884); Brühl, Ann. 235, 19 (1886); Fischer and Speier, Ber. 28, 3254 (1895).

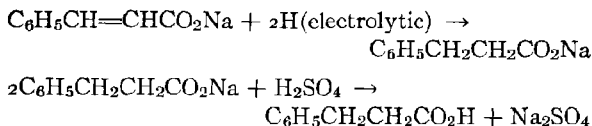
³ Wislicenus and Jensen, Ber. 25, 3449 (1892).

⁴ Claisen, Ber. 23, 977 (1890); Stoermer and Kippe, Ber. 38, 3034 (1905).

⁵ Claisen, Ber. 23, 977 (1890).

XIV

HYDROCINNAMIC ACID



Submitted by A. W. INGERSOLL.

Checked by HENRY GILMAN and L. C. HECKERT.

1. Procedure

A. Apparatus:

THE reduction is carried out in a 7×10 -inch battery jar (Note 1) which is surrounded by a vessel of cold water. The bottom of the battery jar is just covered with mercury which serves as the cathode of the cell. The anode is a coil of heavy sheet lead separated from the catholyte by suspending it in a porous cup. The latter is supported in the battery jar so that it just clears the surface of the mercury (Note 2). The cathode is connected with the circuit by means of a copper wire well insulated with rubber except for one-eighth inch at the end which is immersed in the mercury. Efficient mechanical stirring is provided for the catholyte. The current used for these experiments was drawn from a storage battery delivering 30 volts, through a rheostat and ammeter each capable of carrying 15 amperes. Current may be taken from any source which will supply 80 to 85 ampere-hours at the rate of 5 to 10 amperes. Several reduction cells of the size described may be run at one time by connecting them in series. The diagram given in Org. Syn. 5, 94 shows the arrangement of the apparatus.

B. *Reduction of Cinnamic Acid:*

After the apparatus is assembled, 2 l. of 7-8 per cent sodium sulfate solution (Note 3) is placed in the battery jar and the porous cup is filled to the same level with more of this solution. The stirrer is started and 200 g. (1.35 moles) of a good grade of cinnamic acid (Note 4) is suspended in the catholyte. A solution of 35 g. (0.88 mole) of sodium hydroxide in 150 cc. of water is then added at such a rate as to avoid forming lumps of sodium cinnamate (Note 5). The current is turned on and the rheostat adjusted until a steady current of 5 to 10 amperes is flowing (Note 6). From this point only occasional attention is required. The suspended sodium cinnamate and cinnamic acid gradually dissolve as the reduction proceeds. Portions adhering to the walls of the cell should be worked down with a stirring rod and finally with a little water from a wash-bottle. The liquor inside the porous cup should be kept alkaline by adding very concentrated sodium hydroxide solution at about half-hour intervals (Note 5). About 110 g. (2.7 moles) will be required. The reduction will require 76 to 80 ampere-hours (Note 7); considerable hydrogen is evolved near the end. The temperature need not be controlled (Note 8).

When reduction is complete (Note 7) the cathode liquor is decanted or siphoned from the mercury, filtered from traces of solid matter and acidified with an excess of sulfuric acid (sp. gr. 1.1). The hydrocinnamic acid separates as an oil and solidifies on thorough cooling. The yield of crude product, which contains water and other impurities is 180-200 g. It is purified by distillation under reduced pressure. The product boiling at 194-197°/75 mm. (145-147°/18 mm.) is colorless and melts at 47.5-48°. The yield of distilled acid is 160-180 g. (80-90 per cent of the theoretical amount) depending upon the quality of the cinnamic acid used (Note 4).

2. Notes

1. This is a commercial size. Any sturdy glass vessel of similar dimensions may be used.

2. The lead anode should have about the same surface area as the cathode. The porous cup used was 8×21 cm., but similar sizes will do. A three-legged desiccator plate makes a convenient support for the cup.

3. Any dilute solution of sodium sulfate may be used. If several runs are to be made, the solution recovered from the filtration of the hydrocinnamic acid should be neutralized with sodium hydroxide, diluted if necessary, and used again. Traces of hydrocinnamic acid contained in this solution are thus saved. C. P. chemicals are not necessary.

4. The quality of the cinnamic acid used is important. The yield from a commercial C. P. acid melting at $132.5-133^\circ$ was 86-90 per cent. From a lot melting at $131.5-133^\circ$ obtained by recrystallizing a crude acid with the use of boneblack the yield was 81-83 per cent. With a technical grade of material the yield fell, in some runs, below 60 per cent, the reduction mixture foamed considerably and much high-boiling residue was left on distillation.

5. The addition of too much sodium hydroxide at this point produces a thick sludge which does not stir well. It should be noted that during the reduction two molecular equivalents of sodium hydroxide are produced at the cathode and an equivalent amount of sulfuric acid at the anode.

6. The current may vary somewhat, especially if the anode liquor becomes too dilute or highly acid. The sodium hydroxide solution added to the anolyte should be concentrated so that the diffusion which always occurs will not dilute the catholyte excessively. High amperage shortens the time required but promotes heating. Seven amperes is a convenient rate.

7. The theoretical quantity of current is 72 ampere-hours. It is necessary to pass an excess of 4 to 8 ampere-hours to insure complete reduction. The end of the reduction is reached when a sample of the catholyte on acidification with excess sulfuric acid precipitates an oil and no solid.

8. The reaction is favored by moderately high temperatures. Excessive heating may be avoided by reducing the amperage or by placing cold water in the cooling bath.

9. It may be noted that this process is essentially a sodium amalgam reduction. By the same procedure β -furylacrylic acid was reduced to β -furylpropionic in yields of 60–70 per cent. With suitable modifications it may be applied to the reduction of other substances reducible with sodium amalgam.

3. Methods of Preparation

Hydrocinnamic acid has been prepared by the reduction of cinnamic acid with sodium amalgam,¹ with hydriodic acid at 100°,² and with phosphorus and hydriodic acid;³ by the action of potassium cyanide on β -phenylethyl chloride followed by hydrolysis;⁴ by the acid hydrolysis of benzyl-acetoacetic ester;⁵ and by several other methods of no preparative value. It has also been prepared electrolytically by the reduction of cinnamic acid in alkaline solution on cathodes of lead⁸ and mercury.⁹

¹ Erlenmeyer and Alexejeff, *Ann.* **121**, 375 (1862).

² Glaser, *Zeit. f. Chem.*, **1865**, 111.

³ Gabriel and Zimmerman, *Ber.* **13**, 1680 (1880).

⁴ Fittig and Kiesow, *Ann.* **156**, 249 (1870).

⁵ Merz and Weith, *Ber.* **10**, 758 (1877).

⁶ Conrad, *Ann.* **204**, 176 (1880).

⁷ Conrad and Hodgkinson, *Ann.* **193**, 302 (1878).

⁸ Norris and Cummings, *J. Ind. Eng. Chem.* **17**, 305 (1925).

⁹ Marie, *Compt. rend.* **136**, 1331 (1903).

XV

IODOBENZENE



Submitted by F. B. DAINS and R. Q. BREWSTER.

Check by HENRY GILMAN and J. ROBINSON.

1. Procedure

IN a 1-l. three-neck flask fitted with a mechanical stirrer, reflux condenser and separatory funnel, are placed 381 g. (1.5 moles) of iodine and 400 g. (5.1 moles) of benzene. The mixture is heated to about 50° on a water bath and 275 cc. of nitric acid (sp. gr. 1.50) is added slowly from the separatory funnel; the time required for the addition should be about one and one-quarter hours. A copious evolution of oxides of nitrogen takes place, and the gases are carried off from the upper end of the condenser to an open window or hood. The reaction proceeds smoothly (Note 1) and the temperature rises slowly without the application of heat until the mixture boils gently. When all of the nitric acid has been added, the solution is refluxed for about fifteen minutes. If iodine still remains, more nitric acid should be added slowly to the warm solution until the purple color of the iodine has been discharged and the solution becomes brownish red.

The lower reddish oily layer is separated, mixed with an equal volume of 10 per cent sodium hydroxide solution and steam distilled from a 2-l. flask until no more oil passes over. Towards the end of the distillation a yellow solid begins to collect in the receiver; this consists of nitro compounds, which are removed by vigorously stirring the oil for about three hours with 20 cc. of concentrated hydrochloric acid, 300 cc. of water and 200 g. of iron filings in a 2-l. flask connected with a reflux condenser.

The mixture is allowed to cool and is then filtered. The filtrate is rendered distinctly acid to congo red with hydrochloric acid and again distilled with steam. The oil so obtained is separated and distilled under normal pressure with the use of a fractionating column (Note 2). The fraction boiling at 180–190° is redistilled and the pure compound is collected at 184–186°. The yield is 523–531 g. (86–87 per cent of the theoretical amount) (Note 3).

2. Notes

1. The reaction proceeds smoothly without stirring; however, the time of addition is decreased somewhat by stirring. Ordinary rubber stoppers may be used; although they are somewhat attacked, this is not sufficiently serious to warrant any special apparatus. In very large runs it may be desirable to use stoppers made from asbestos paper and water glass (Org. Syn. 5, 9). Rubber stoppers have been used in a run five times the size of that described.

2. A good separation is obtained by means of a 500-cc. modified Claisen flask (Org. Syn. 1, 40) without the use of diminished pressure.

3. Iodobenzene prepared by this procedure may contain traces of nitro compounds. The test for these is to reduce a sample with stannous chloride (or tin) and hydrochloric acid, and treat the resulting acid solution in the cold with a solution of sodium nitrite. If a phenolic odor is obtained on boiling the solution, nitro compounds are still present. A more delicate test can be made by adding the reduced solution, after treatment with sodium nitrite, to an alkaline solution of β -naphthol; an azo dye is formed if nitro compounds were originally present.

3. Methods of Preparation

The present method is essentially that of Datta and Chatterjee.¹ Oxidizing agents other than nitric acid have been used in the preparation of iodobenzene from benzene and iodine, but

¹ Datta and Chatterjee, J. Am. Chem. Soc. **39**, 437 (1917).

no one of them appears to be as effective and as convenient as nitric acid. Those that have been used are iodic acid,² fuming sulfuric acid,³ mercuric oxide⁴ and ferric chloride.⁵ Other methods of preparative interest are the diazo reaction starting with aniline;⁶ the reaction between benzene, iodine monochloride and aluminum chloride;⁷ benzene, sulfur iodide and nitric acid;⁸ and phenylmagnesium bromide and iodine.⁹

² Kekulé, Ann. **137**, 162 (1866); Klages and Liecke, J. prakt. chem. (2) **61**, 311 (1900).

³ Rupp, Ber. **29**, 1629 (1896); Neumann, Ann. **241**, 84 (1887).

⁴ Weselsky, Ann. **174**, 99 (1874).

⁵ Meyer, Ann. **231**, 195 (1885); J. prakt. Chem. (2) **34**, 504 (1886).

⁶ Griess, Jahresber. **1866**, p. 477.

⁷ Greene, Bull. soc. chim. **36**, 234 (1881).

⁸ Edinger and Goldberg, Ber. **33**, 2875 (1900).

⁹ Datta and Mitter, J. Am. Chem. Soc. **41**, 288 (1919).

XVI

LEVULINIC ACID



Submitted by B. F. MCKENZIE.

Checked by H. T. CLARKE and R. PHILLIPS.

1. Procedure

To a solution of 500 g. (1.46 moles) of cane sugar (Note 1) in 1 l. of water in a 2-l. flask is added 250 cc. of concentrated hydrochloric acid (sp. gr. 1.16). The flask is heated on a steam-bath for twenty-four hours, during which time considerable carbonization takes place. The black solid is filtered off with suction and washed with 300 cc. of water. The filtrate is placed in a large evaporating dish on a steam-bath and allowed to evaporate overnight. The black solid residue obtained on the following morning is ground to a powder and placed in a folded filter paper of 34 cm. diameter. This is placed in a 25-cm. funnel fitted with a water-cooled 12-l. flask as described in Org. Syn. 2, 49. The solid is extracted with 500 cc. of ether for six to eight hours. The ether is distilled and the residue (Note 2) fractionated under reduced pressure. The fraction distilling at 150–160°/15 mm. or 135–140°/10 mm. forms a rather dark liquid which does not completely solidify on cooling.

On redistillation under reduced pressure a fraction boiling over a range of not more than 2° (e.g., 137–139°/10 mm.) is obtained with very little loss; this fraction solidifies almost completely at 30°. The yield is 72–76 g. (22–23 per cent of the theoretical amount).

2. Notes

1. Equally good results may be obtained with starch; the mixture, however, must be warmed more slowly as it is apt to foam at the outset.

2. When larger quantities of levulinic acid are to be prepared it has been found by the checkers to be more convenient to fractionally distil the first filtrate under reduced pressure, without evaporating to dryness and extracting with ether. In this case a considerable quantity of tarry residue remains in the distilling flask. The yields are equally good.

3. Methods of Preparation

The only practical methods for preparing levulinic acid depend upon the action of mineral acids upon carbohydrates, a reaction discovered by Grote and Tollens,¹ who heated cane sugar with dilute sulfuric acid. The method above described is essentially that of Conrad,² descriptions of which frequently have appeared³ in the subsequent literature. The use of vacuum distillation was suggested by Kent and Tollens.⁴ Levulinic acid has also been prepared from starch by the action of hydrochloric acid.⁵

¹ Grote and Tollens, *Ann.* **175**, 181 (1875); **206**, 226 (1880).

² Conrad, *Ber.* **11**, 2177 (1878).

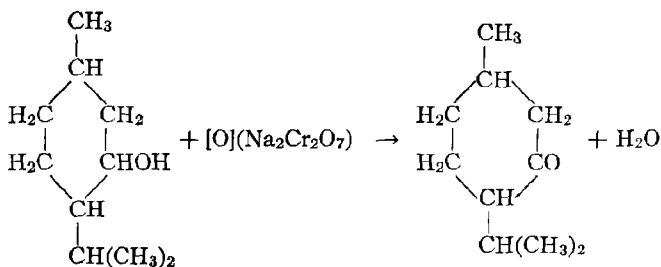
³ Fittig and Wolff, *Ann.* **208**, 104 (1881); Neugebauer, *Ann.* **227**, 97 (1885); Seissl, *Ann.* **249**, 272 (1888).

⁴ Kent and Tollens, *Ann.* **227**, 229, Note 2 (1885).

⁵ Rischbieth, *Ber.* **20**, 1773 (1887).

XVII

L-MENTHONE



Submitted by L. T. SANDBORN.

Checked by H. T. CLARKE and ROSS PHILLIPS.

1. Procedure

IN a 1-l. round-bottom flask provided with a mechanical stirrer is placed 120 g. (0.4 mole) of crystallized sodium dichromate (or an equivalent amount of potassium dichromate), and to this is added a solution of 100 g. (0.97 mole) of concentrated sulphuric acid (sp. gr. 1.84) in 600 cc. of water. To this mixture 90 g. (0.57 mole) of menthol (crystals, m. p. 41–42°) is added in three or four portions and the mixture stirred (Note 1). Heat is evolved and the temperature of the mixture rises to about 55° (Note 2). As soon as the reaction is complete the temperature falls. The oil is mixed with an equal volume of ether, separated in a separatory funnel, and washed with three 200-cc. portions of 5 per cent sodium hydroxide solution (Note 3). The ether is then removed by distillation and the residue distilled under reduced pressure, the menthone being collected at 98–100°/18 mm. If distilled under atmospheric pressure it boils at 204–207°. The yield is 74–76 g. (83–85 per cent of the theoretical amount).

2. Notes

1. On addition of the menthol a black spongy mass forms which softens as the temperature rises and finally forms a dark-brown oil.

2. The temperature may not reach 55° , in which case the mixture may be warmed gently with a small flame. In case the reaction is slow in starting, gentle heating with a small flame is advantageous.

3. The oil, which is dark brown before washing with sodium hydroxide, becomes light yellow. If three washings are not sufficient to remove the dark color another portion of sodium hydroxide solution is used.

3. Methods of Preparation

l-Menthone can be made by the oxidation of rhodinol with a chromic-sulphuric acid mixture.¹ A Sabatier-Senderens reduction of thymol gives a mixture containing 30 per cent menthone.² *l*-Menthone is also obtained by treating menthol with copper at 300° .³ The method used in these directions is that of Beckmann.⁴

¹ Bouveault, Bull. soc. chim. (3) **23**, 464 (1900).

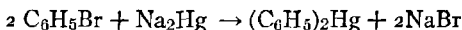
² Pickard and Littlebury, J. Chem. Soc. **101**, 113 (1912).

³ Neave, J. Chem. Soc. **101**, 513 (1912).

⁴ Beckmann, Ann. **250**, 325 (1889).

XVIII

MERCURY DIPHENYL



Submitted by H. O. CALVERY.

Checked by FRANK C. WHITMORE and R. W. BEATTIE.

1. Procedure

In a 1-l. round-bottom flask fitted with a reflux condenser are placed 900 g. of 3 per cent sodium amalgam (Note 1), 180 g. (1.15 moles) of bromobenzene, 200 cc. of dry toluene or dry xylene, and 10 cc. of ethyl acetate. The mixture is refluxed with frequent shaking for twelve hours in an oil bath at 130°.

The mixture is transferred (Hood) (Note 5) while still hot to a fluted filter paper in a 20-cm. glass funnel, leaving behind as much mercury as possible (Note 2). The funnel is made part of a special extraction apparatus as described in Org. Syn. 2, 49. The mercury diphenyl is extracted with 600 cc. of boiling benzene for about ten hours (Note 3).

The solution is distilled under reduced pressure on an oil bath, the temperature of which is raised to 110° near the end of the distillation. The solid residue left in the flask after removal of the solvent is taken out and washed until nearly white with 95 per cent alcohol which has been cooled in an ice bath. This requires about four washings of 50 cc. of alcohol each (Note 4). The yield is 65-75 g. (32-37 per cent of the theoretical amount). The melting point is 121-123°.

2. Notes

1. For the preparation of sodium amalgam see Org. Syn. 7, 89.
2. Care must be taken to remove all the mercury diphenyl;

but if too much mercury is removed, it may break the filter paper or weight it down so that the benzene vapors cannot rise around it. It is sometimes best to put stirring rods down around the sides of the paper to insure a free path for the benzene vapors.

3. In some cases the extraction may not be complete in this length of time.

4. Some mercury diphenyl may be recovered by combining the washings from several runs.

5. Mercury diphenyl is very poisonous. The vapors of the benzene solution must not be breathed.

3. Methods of Preparation

Mercury diphenyl has been prepared in a number of ways. The most important methods are: by the action of sodium on a mixture of bromobenzene and mercuric chloride;¹ from sodium amalgam and phenyl mercuric iodide;² by the interaction of phenyl mercuric bromide and potassium sulfide² or phenyl mercuric acetate and sodium stannite;³ from phenyl magnesium bromide and mercuric chloride;⁴ by the action of phenyl hydrazine on mercury compounds;⁵ from mercuric chloride and phenyl arsenious oxide;⁶ and from diphenyl mercuric ammonium acetate and sulfur compounds.⁷

¹ Michaelis and Reese, Ber. **15**, 2877 (1882).

² Dreher and Otto, Ber. **2**, 542 (1869).

³ Dimroth, Ber. **35**, 2853 (1902).

⁴ Pfeiffer and Truskier, Ber. **37**, 1127 (1904).

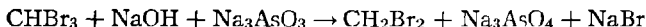
⁵ Fischer and Erhardt, Ann. **199**, 332 (1879).

⁶ Fraenkel, Arzneimittelsynthese, 4th ed. (1919), 661.

⁷ Pesci, Gazz. chim. ital. **39**, I, 150 (1909).

XIX

METHYLENE BROMIDE



Submitted by W. W. HARTMAN and E. E. DREGER

Checked by FRANK C. WHITMORE and C. J. KORPL.

1. Procedure

IN a 2-l. round-bottom flask placed on a steam bath and fitted with a stirrer, a separatory funnel, and a reflux condenser is placed 540 g. (1.9 moles) of commercial (88 per cent) bromoform (Note 1). There is then added 10 cc. of a solution of sodium arsenite made by dissolving 230 g. (1.16 moles) of c. p. arsenious oxide and 445 g. (11 moles) of sodium hydroxide in 1.4 l. of water. The mixture is warmed gently to start the reaction, and then the remainder of the sodium arsenite solution is added during about one hour at such a rate that the solution refluxes gently. When the addition is complete, the flask is heated for four hours on the steam bath. The reaction mixture is distilled with steam, the lower layer of methylene bromide separated, and the water layer extracted once with 100 cc. of ether (Note 2). The methylene bromide is dried with 10 g. of calcium chloride and distilled. The yield of slightly yellow liquid boiling at 97–100° is 290–300 g. (88–90 per cent of the theoretical amount).

2. Notes

1. The commercial bromoform used contained 12 per cent of alcohol. Its specific gravity was 2.59/25° as compared with 2.88/25° for pure bromoform.

2. The chief function of the extraction is to collect the fine droplets of methylene bromide which remain in the water layer.

3. Methods of Preparation

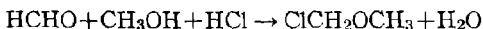
Methylene bromide has been prepared by the reaction of bromine with methylene iodide,¹ and by the action of bromine on methyl bromide ² at 250°. The present method is adapted from the preparation of methylene iodide described in Org. Syn. 1, 57.

¹ Butlerow, Ann. 111, 251 (1859).

² Steiner, Ber 7, 507 (1874)

XX

MONOCHLOROMETHYL ETHER



Submitted by C. S. MARVEL and P. K. PORTER.

Checked by H. T. CLARKE and E. R. TAYLOR.

1. Procedure

IN a 2-l. round-bottom flask fitted with a stopper carrying a reflux condenser and a glass tube reaching nearly to the bottom of the flask are placed 350 g. (10.9 moles) of methyl alcohol and 900 g. of technical formalin containing 252 g. (8.4 moles) of formaldehyde (Note 1).

A rapid stream of hydrogen chloride (Note 2) is run into the mixture, which is cooled with running water. In about two hours a layer of chloromethyl ether begins to appear. The stream of hydrogen chloride is continued for two or three hours longer until the solution is saturated. The layer of chloromethyl ether is then separated. The water layer is saturated with calcium chloride (Note 3) and more ether separates. This is added to the main portion which is then dried over calcium chloride and fractionally distilled. The yield of a product boiling at 55–60° is 580–600 g. (86–89 per cent of the theoretical amount based on the formaldehyde).

2. Notes

1. The following table showing the relation between the density of formalin solutions and their formaldehyde content has been found useful. It is copied from Beilstein's Handbuch

der Organischen Chemie, 4th Ed., Julius Springer, Berlin, 1918.
Vol. I, page 561.

$d \frac{18}{4}$	g. CH ₂ O in 100 cc.	g. CH ₂ O in 100 g.
1.0054	2.24	2.23
1.0126	4.66	4.60
1.0311	11.08	10.74
1.0410	14.15	13.59
1.0568	19.89	18.82
1.0719	25.44	23.73
1.0853	30.17	27.80
1.1057	37.72	34.11
1.1153	41.87	37.53

2. The hydrogen chloride was generated by the method described in Org. Syn. 2, 30. About 390-420 g. of hydrogen chloride is required for saturation.

3. Chloromethyl ether is soluble in the aqueous hydrochloric acid used so that the salting out with calcium chloride is necessary to obtain the maximum yield.

3. Methods of Preparation

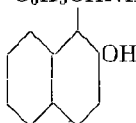
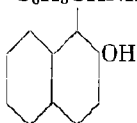
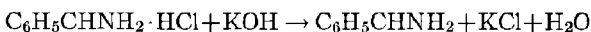
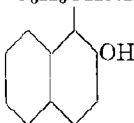
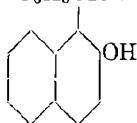
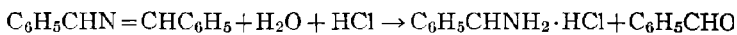
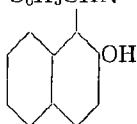
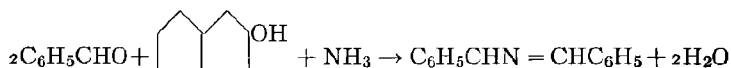
Monochloromethyl ether has been prepared by saturating an aqueous solution of formaldehyde and methyl alcohol with hydrogen chloride¹ and by saturating a solution of trioxymethylene in methyl alcohol with hydrogen chloride.² The method which is described in the procedure is essentially that developed by Henry.³

¹ Henry, Ber. 26, 933 (1893); Favre, Bull. soc. chim. (3) 11, 1095 (1894); Litterscheid and Thimme, Ann. 334, 10 (1904).

² Wedekind, Ger. pat. 135,310 (Chem. Zentr. 1902 (II), 1164); Ber. 36, 1384 (1903); Houben and Arnold, Ber. 40, 4307 (1907); Litterscheid, Ann. 330, 109 (1904); Reychler, Bull. soc. chim. (4) 1, 1195 (1907).

³ Henry, Ber. 26, 933 (1893).

XXI

 β -NAPHTHOL PHENYLAMINOMETHANE

Submitted by M. BETTI.

Checked by C. S. MARVEL and G. S. HIERS.

1. Procedure

IN a 1-l. round-bottom flask is placed a cold solution of 144 g. (1 mole) of β -naphthol in 200 cc. of 95 per cent alcohol (Note 1). To this solution is added first 212 g. (2 moles) of freshly distilled benzaldehyde (which has been previously freed from acid by shaking with 5 per cent sodium carbonate solution) and then about 200 cc. of 95 per cent alcohol which has been saturated with ammonia at room temperature. The solution becomes red and warms up spontaneously. The flask is stoppered and allowed to

stand for two hours. Then the stopper is removed, and the excess ammonia is allowed to escape. After about twelve hours, the condensation product, which has separated as white needles, is filtered with suction and washed with 50 cc. of alcohol. The mother liquors on standing for three days deposit an additional quantity of the condensation product (Note 2). The yield is 284-306 g. (85-92 per cent of the theoretical amount) of a product which melts at 148-150°.

The condensation product thus obtained is introduced into a 5-l. round-bottom flask arranged for steam distillation, and treated with three to four times its volume of 20 per cent hydrochloric acid. The mixture is steam distilled to remove all benzaldehyde formed by the hydrolysis (about two hours) (Note 3). Meanwhile, an abundant flocculent precipitate of light pink or white needles separates. The mixture in the flask is cooled thoroughly and filtered with suction. The yield is 240-260 g. (84-91 per cent of the theoretical amount) of a product which melts at 190-220° with decomposition (Note 4).

The hydrochloride thus obtained varies from pure white to a light red in color, depending on the purity of the original reagents and on the length of time required for the hydrolysis. However, the color does not interfere with isolation of a pure white free base when the salt is treated with alkali. The salt is somewhat more stable than the free base, and if the reagent is to be stored for some time, it should be kept in this form.

In order to obtain the amine, 200 g. of finely divided hydrochloride is placed in a 1500-cc. beaker and stirred into a smooth paste with 300 cc. of water. To this is added 50 g. of crushed ice, and the mixture is cooled in an ice bath (Note 5). Then 750-800 cc. of 25 per cent aqueous potassium hydroxide is added slowly with stirring until the hydrochloride dissolves. The cold solution is transferred to a separatory funnel and extracted with four 300-cc. portions of ether. The combined ether extract is dried overnight with 50 g. of anhydrous sodium sulfate, filtered, and concentrated to about 300 cc. On cooling the solution in an ice bath, the amine crystallizes and is filtered with suction. The first crop of crystals weighs 112-115 g. Further concen-

tration of the mother liquors to about 100 cc. and cooling yields 14-18 g. more of the product (Note 6). The total yield is 127-131 g. (73-75 per cent of the theoretical amount) of a product which melts at 124-125° (Note 7). If desired, it may be purified by dissolving in an excess of dry ether, evaporating the excess of solvent, and allowing the amine to crystallize. Thus, 24.5 g. of the amine, when dissolved in 800 cc. of dry ether and the solution filtered and evaporated in a current of air to 150 cc., yields 18-19 g. of product, melting at 124-125°.

2. Notes

1. It is usually necessary to warm the alcohol in order to dissolve the β -naphthol. This solution is then cooled before the addition of the benzaldehyde.

2. Even after three days' standing, the reaction is not entirely complete, and an additional 8-10 g. of product may be obtained by allowing the mother liquors to stand for another three or four days.

3. Sometimes when the distillation is carried on for too long a period, the hydrochloride coagulates to a hard red mass. If this happens, the product may be purified by crystallization from about 15 per cent hydrochloric acid. Even the deeply colored hydrochloride yields a colorless amine.

4. The hydrochloride is almost insoluble in cold water. It is slightly hydrolyzed by boiling water.

5. The temperature should be kept below 20° during the addition of the alkali, or the product is decomposed and ammonia is evolved.

6. A small additional amount of impure product may be obtained by evaporating the mother liquors further and cooling the solution. This product amounts to only a few grams and needs to be purified by recrystallization from ether.

7. This amine is of interest because it is readily resolved with tartaric acid to give the pure dextro and levo isomers.¹

¹ Betti, *Gazz. chim. ital.* **36**, II, 392 (1906).

These optically active bases are very useful in the resolution of various types of racemic substances.

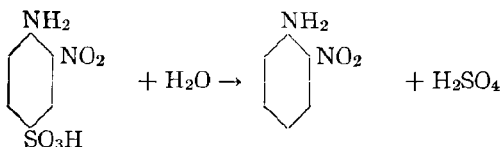
3. Methods of Preparation

β -Naphthol phenylaminomethane has been prepared only by the method outlined in the procedure.²

² Betti, Gazz. chim. ital. **31**, I, 385 (1901).

XXII

o-NITROANILINE



Submitted by LOUIS EHRENFELD and MILTON PUTERBAUGH.
 Checked by ROGER ADAMS and S. V. PUNTAMBEKER.

1. Procedure

In a 3-l. round-bottom flask fitted with a reflux condenser are placed 218 g. (1 mole) of coarsely powdered technical *o*-nitroaniline-*p*-sulfonic acid, and a hot mixture of 775 cc. of concentrated sulfuric acid (sp. gr. 1.84) and 950 cc. of water (Note 1). Heat is applied and the mixture is refluxed gently for an hour after solution is practically complete (total about three hours). The resulting dark solution is allowed to cool and is poured slowly into 12 l. of cold water in a crock (Note 2).

After cooling, the dense orange-yellow precipitate is filtered with suction. This crop of crystals after air-drying weighs about 70 g. and melts at 68–70°. The filtrate is returned to the crock and made slightly alkaline with 50 per cent sodium hydroxide solution (about 2.25 l.). It is then made barely acid to litmus with sulfuric acid. This neutralization will produce considerable heat and the mixture should be thoroughly cooled before filtering. This second crop of crystals weighs about 22–25 g. and melts at 69–70.5°. The total crude yield is 90–95 g.

The two crops of crystals may be combined for recrystallization from boiling water, using 1 l. for each 9 g. The hot solution

is filtered quickly and the filtrate is cooled thoroughly and filtered with suction. The crystals are dried at 50°. The product melts at 69-71°. An alternate method of purification is to dissolve the crude product in about 250 cc. of 95 per cent alcohol, filter the solution, dilute with 1 l. of hot water and warm on a steam bath if a precipitate forms. On cooling this solution the product separates in orange-brown needles, and is filtered and air dried. The yield is about 78 g. (56 per cent of the theoretical amount), m.p. 69.5-70.5°.

2. Notes

1. If cold, diluted acid is used, stirring must be employed during the heating to prevent caking and consequent charring.

2. The dark solution may be poured slowly over sufficient ice to half-fill a 16-l. (4-gal.) crock. A good yield was obtained in this way, but at this point the temperature is not likely to rise much and the use of cold water is cheaper and sufficiently satisfactory.

3. Methods of Preparation

o-Nitroaniline has been obtained together with some *p*-nitroaniline in the nitration and subsequent hydrolysis of acetanilide¹ and of benzanilide;² by the sulfonation, nitration and subsequent hydrolysis of oxanilide³ and of acetanilide;⁴ by the nitration of aniline and separation of the mixture of isomers;⁵ and by heating a mixture of *o*-chloronitrobenzene with ammonium acetate.⁶

¹ Walker and Zincke, Ber. **5**, 114 (1872); Remsen and Graham, Am. Chem. J. **11**, 320 (1889); Weida, Am. Chem. J. **19**, 547 (1897); Pokorry, Bull. Soc. Indus. Mulhouse **1894**, 280 [Chem. Zentr. **1894**, II, 556].

² Lellmann, Ann. **221**, 6 (1883).

³ Ger. pat. 65,212; 66,060 [Frdl. **3**, 44, 45 (1892)].

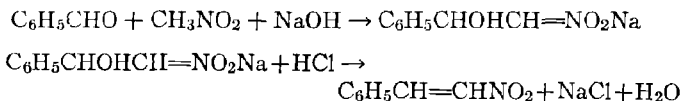
⁴ Nietzki and Benckiser, Ber. **18**, 295 (1885); Turner, Ber. **25**, 986 (1892); Sakellarios, Ber. **58**, 2286 (1925).

⁵ Bruns, Ber. **28**, 1954 (1895).

⁶ Brit. pat. 169,688 [C. A. **16**, 721 (1922)].

XXIII

NITROSTYRENE



Submitted by DAVID E. WORRALL.

Checked by C. S. MARVEL and W. II. LYCAN.

1. Procedure

IN a 6-l. wide-mouth bottle, packed in a pail with a freezing mixture of ice and salt and fitted with a mechanical stirrer, a thermometer and a separatory funnel, are placed 305 g. (5 moles) of nitromethane (Org. Syn. 3, 83) 530 g. (5 moles) of benzaldehyde (Note 1) and 1000 cc. of methyl alcohol. A solution of sodium hydroxide is prepared by dissolving 210 g. (5.25 moles) of caustic soda in approximately an equal volume of water and cooling. It is then diluted to 500 cc. with ice and water, poured into the funnel, and added with stirring to the nitromethane mixture at such a rate that the temperature is kept at 10–15° (Notes 2 and 3).

A bulky white precipitate forms rapidly during the addition of the alkali. The mixture gets so thick that stirring becomes difficult and it may be advisable to add 100 cc. more of methyl alcohol. After fifteen minutes' standing, the pasty mass is converted to a clear solution by the addition of 3–3.5 l. of ice water containing crushed ice (Note 4). Hydrochloric acid (made by diluting 1000 cc. of concentrated hydrochloric acid with 1500 cc. of water) is placed in a 15-l. mixing jar and the reaction mixture run into this from the separatory funnel at such a rate that the stream just fails to break into drops (Note 5). A pale

yellow crystalline mass separates almost immediately as the alkaline solution comes in contact with the acid. After the stirring is stopped, the solid settles to the bottom of the jar. The major part of the cloudy liquid layer is removed by decantation, and the residue filtered by suction and washed with water until free from chlorides. This product is freed from all but a negligible amount of water by melting in a beaker immersed in hot water. Two layers are formed and on cooling again the lower layer of nitrostyrene freezes; the water may then be poured off. The crude nitrostyrene is purified by dissolving in 420 cc. of hot ethyl alcohol (Note 6), filtering the solution into a warm suction flask to remove solid impurities, and then cooling until crystallization is complete. The yield of crude product melting at $56-58^{\circ}$ is 650-670 g. The yield of recrystallized nitrostyrene melting sharply at $57-58^{\circ}$ is 600-620 g. (80-83 per cent of the theoretical amount). The whole procedure, including purification, can be done in a day.

2. Notes

1. Technical benzaldehyde which had been washed with sodium carbonate solution, dried and distilled under reduced pressure, was used in this preparation.

2. The first few cubic centimeters of sodium hydroxide solution should be added cautiously to the nitromethane mixture since, after a short induction period, there is a considerable evolution of heat and the temperature may rise from -10° to 30° or even higher in spite of good stirring. If necessary, this rise in temperature is easily checked by adding a handful of crushed ice directly to the mixture. After this initial reaction the rest of the alkali may be added more rapidly.

3. The condensation induced by sodium hydroxide is almost instantaneous above 10° . The procedure may be interrupted with safety after the addition of alkali, and the product will not change on standing overnight in an ice chest.

4. After the product has been dissolved in water the resulting alkaline solution is much more sensitive and should be used up as rapidly as possible and the temperature kept below 5° .

5. The alkaline solution must be added slowly to the acid, for the reverse procedure always forms an oil containing a saturated nitro alcohol. A large excess of acid at room temperature is used, conditions which facilitate the formation of the desired unsaturated nitro compound.

6. The vapors of hot solutions of nitrostyrene are very irritating to the eyes and nose, while the skin of the face is sensitive to the solid substance.

3. Methods of Preparation

Nitrostyrene has been obtained in small yields by a number of methods, but the only practical methods of preparation start with benzaldehyde and nitromethane. The condensation was first accomplished by heating nitromethane and benzaldehyde in sealed tubes with anhydrous zinc chloride.¹ Good results are obtained by adding small amounts of a primary aliphatic amine to a mixture of nitromethane and benzaldehyde,² but it takes a number of days for the reaction to go to completion. Undoubtedly the best method is the use of alkali to condense benzaldehyde and nitromethane, as first discovered by Thiele.³

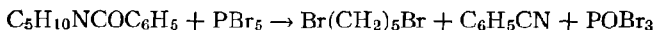
¹ Priebis, *Ann.* **225**, 320 (1884).

² Knoevenagel and Walter, *Ber.* **37**, 4507 (1904).

³ Thiele, *Ber.* **32**, 1293 (1899); Thiele and Haeckel, *Ann.* **325**, 7 (1902).

XXIV

PENTAMETHYLENE BROMIDE



Submitted by J. VON BRAUN.

Checked by J. B. CONANT and J. S. ANDREWS.

1. Procedure

In a 500-cc. Claisen distilling flask is placed 80 g. (0.42 mole) of benzoyl piperidine (p. 16). To this is added with cooling 115 g. (0.43 mole) of phosphorus tribromide; this results in the formation of a light-colored solution. With careful cooling, this solution is treated, with shaking, with 65 g. of bromine (0.81 mole). The flask is now connected for vacuum distillation and the solution heated gradually for a few minutes until the rapid evolution of gas ceases. The product is then vacuum distilled. At about 70°/20 mm. a mixture of pentamethylene bromide, phosphorus oxybromide and benzonitrile begins to distil over into the receiver; a yellow solid collects in the condenser. This is then followed by a black decomposition product, at which point the distillation is stopped. The distillate is poured onto ice and allowed to stand in order to decompose the phosphorus oxybromide, a process which requires about one hour if carried out in a flask fitted with a reflux condenser and mechanical stirrer. The heavy oil is removed from the water and consists of pentamethylene bromide and benzonitrile. This oily layer is treated with 125 cc. of 40 per cent hydrobromic acid solution and boiled under a reflux condenser with vigorous stirring for about three hours in order to hydrolyze completely the benzonitrile to benzoic acid (Note 1). The mixture is then distilled with steam using an air condenser between the distillation flask

and the receiving flask and fitting to the latter a reflux condenser cooled with water. This apparatus is necessary to avoid clogging of the condenser tubes with the benzoic acid. The pentamethylene bromide is separated from the water layer, washed with sodium carbonate, dried over calcium chloride and distilled under reduced pressure. The product boils at $108-110^{\circ}/20$ mm. and amounts to 63-70 g. (65-72 per cent of the theoretical amount).

2. Notes

1. It has been suggested in the literature¹ that the benzonitrile may be removed from the pentamethylene bromide by shaking repeatedly with concentrated sulfuric acid. This did not prove satisfactory in the laboratory on account of the formation of emulsions. When a solvent such as petroleum ether is added, the emulsions may be avoided but the yield of final product is always lower than that obtained by the method described.

3. Methods of Preparation

Pentamethylene bromide has been prepared by the action of fuming hydrobromic acid on pentamethylene glycol,² or 1,5-diphenoxypentane;³ by the action of hydrobromic acid on an acetic acid solution of 1,5-di-isoamyloxypentane;⁴ and by the action of phosphorus pentabromide on benzoyl piperidine.⁵

¹ Dox and Yoder, *J. Am. Chem. Soc.* **43**, 1368 (1921); Clarke, *J. Chem. Soc.* **103**, 1703 footnote (1913).

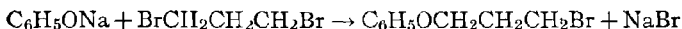
² Gustavson and Demjanoff, *J. prakt. Chem.* (2) **39**, 542 (1889); Haworth and Perkin, *Ber.* **26**, 2247 (1893); Hochstetter, *Monatsh.* **23**, 1071 (1902).

³ v. Braun and Steindorff, *Ber.* **38**, 960 (1905).

⁴ Hamonet, *Compt. rend.* **138**, 1611 (1904); *Bull. soc. chim.* (3) **33**, 530 (1905).

⁵ v. Braun, *Ber.* **37**, 3211 (1904); J. v. Braun and Steindorff, *ibid.* **38**, 2338 (1905); *Ger. pat.* 164, 365 [*Chem. Zentr.* **1905**, II, 1564]; Clarke, *J. Chem. Soc.* **103**, 1703 footnote (1913); Dox and Yoder, *J. Am. Chem. Soc.* **43**, 1368 (1921).

XXV

 γ -PHENOXYPROPYL BROMIDE

Submitted by C. S. MARVEL and A. L. TANENBAUM.

Checked by H. T. CLARKE and C. J. MALM.

1. Procedure

In a 5-l. round-bottom flask, fitted with a stopper carrying a long reflux condenser, a mechanical stirrer (Note 1) and a separatory funnel, are placed 2 l. of water (Note 2), 1 kg. (4.95 moles) of trimethylene bromide (Org. Syn. 1, 8) (Note 3) and 370 g. (3.9 moles) of phenol. The stirrer is started and the mixture is heated to boiling. To the boiling solution is added a solution of 150 g. (3.75 moles) of sodium hydroxide in 500 cc. of water at such a rate that all is added in about one hour. The mixture is refluxed for five to six hours longer to complete the reaction, then cooled and the upper water layer separated and discarded. The lower layer consists of trimethylene bromide, phenoxypropyl bromide and diphenoxypropane. This mixture is distilled under reduced pressure, using a Claisen flask with a modified side arm (Org. Syn. 1, 40). The first fraction is collected up to 136°/20 mm. and consists of water and recovered trimethylene bromide with a little phenoxypropyl bromide (Note 4). The water is separated and discarded. The recovered trimethylene bromide weighs 340-450 g. (Note 5). The next fraction is pure phenoxypropyl bromide which boils at 136-142°/20 mm. The yield is 495-600 g. (84-85 per cent of the theoretical amount based on the trimethylene bromide actually used) (Note 6). On cooling the phenoxypropyl bromide, it crystallizes to a white solid, m.p. 7-8°. A small amount (50-

80 g.) of diphenoxypropane is left as a residue in the distilling flask.

2. Notes

1. The reaction may be run without stirring but a longer period of refluxing is necessary and the yield is lower.

2. If less water is used in the reaction mixture, sodium bromide separates.

3. The large excess of trimethylene bromide must be used in order to avoid the formation of large amounts of diphenoxypropane.

4. Phenoxypropyl bromide attacks rubber stoppers quite readily and the side arm of the distillation flask should be set in (Org. Syn. 1, 40) in order to avoid contamination of the distillate.

5. The use of recovered trimethylene bromide does not result in as good a yield of phenoxypropyl bromide, because a little phenoxypropyl bromide is already present and during the reaction is converted to diphenoxypropane.

6. Phenoxyethyl bromide may be made in a similar manner. Two kilos of ethylene bromide, 285 g. of phenol and 2 l. of water, upon treatment with 375 g. of sodium hydroxide, yield 960-970 g. of phenoxyethyl bromide (54-57 per cent of the theoretical amount) boiling at 125-130°/18 mm.

3. Methods of Preparation

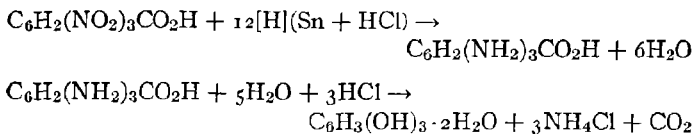
γ -Phenoxypropyl bromide has been prepared by the action of sodium phenoxide on trimethylene bromide in alcohol solution.¹ The method described in the procedure has been published by Marvel and Tanenbaum.²

¹ Lohmann, Ber. **24**, 2631 (1891), Salonina, Ber. **26**, 2987 (1893), v. Braun and Beschke, Ber. **39**, 4120 (1906)

² Marvel and Tanenbaum, J. Am. Chem. Soc. **44**, 2647 (1922).

XXVI

PHLOROGLUCINOL



Submitted by H. T. CLARKE and W. W. HARTMAN.
Checked by C. S. MARVEL and A. T. BLOMQUIST.

1. Procedure

To 225 g. (0.87 mole) of crude 2,4,6-trinitrobenzoic acid (Notes 1 and 2), prepared as described in Org. Syn. 2, 95, is added 1800 cc. of concentrated hydrochloric acid (sp. gr. 1.17) in a 5-l. flask provided with a reflux condenser, the inner tube of which is 15-20 mm. in diameter. To this mixture is added 825 g. (7.0 moles) of granulated tin in small portions, the reaction being started after the addition of 30-40 g. of the tin by immersing the flask in a hot-water bath (Note 3). The rest of the tin is added through the condenser at such a rate that the reaction proceeds briskly. It is advisable to carry out this reaction under a hood since hydrogen chloride is apt to escape at the beginning of the reaction. The mixture is finally heated on a steam bath for an hour in order to complete the reaction, and is then filtered hot through glass wool in order to remove unreacted tin.

The filtrate is made up to exactly 2 l. and a 50 cc. sample titrated with sodium hydroxide solution of known concentration (35-40 per cent is a suitable strength). The volume of alkali necessary to produce a slight permanent precipitate is noted (it usually requires 6-8 cc. of 40 per cent alkali). More alkali is run in until the liquid is neutral to litmus paper: this second value

represents the acid combined with tin. To the filtrate in the 5-l. flask is added 1 kilo of cracked ice, and then sufficient alkali to neutralize the free acid as well as 60 per cent of that combined with the tin (about 800 cc. of 40 per cent sodium hydroxide is required). The mixture is diluted, without filtering, to 6 l. and boiled in a 12-l. flask under a reflux condenser in an atmosphere of coal gas (Note 4) for twenty hours. The precipitate is then filtered off and washed very thoroughly with boiling water (2-3 l. of water) and the combined filtrates concentrated to 3 l. This is then rendered slightly acid to litmus with hydrochloric acid, and chilled to 0°, when crystals of phloroglucinol separate. This crop is filtered off; it should weigh 70-80 g. It is then dissolved in 700 cc. of hot water, filtered, and allowed to crystallize at 0°. In this way 65-75 g. (46-53 per cent of the theoretical amount) of almost colorless (Note 5) phloroglucinol dihydrate melting at 217-218° is obtained.

2. Notes

1. It is unnecessary to remove the small amount of trinitrotoluene with which the crude trinitrobenzoic acid is contaminated, since it has been found that no trace of the methyl homologue of phloroglucinol is obtained on treating trinitrotoluene in the above manner.

2. An equivalent quantity of 1,3,5-trinitrobenzene may be employed in place of trinitrobenzoic acid with exactly the same result; but as the most convenient method of preparing trinitrobenzene in the laboratory is through trinitrobenzoic acid, nothing is gained by the substitution.

3. In carrying out the reduction, care must be taken that not more than 5 per cent of the tin is added before the reaction starts, otherwise the interaction begins with such violence that the product may be lost. The reaction may be readily checked by immersion of the flask in water. The application of wet towels to the upper half of the flask is often of great assistance to condensation while only slightly checking the reaction itself.

4. Coal gas is recommended as being the most convenient

inert gas in which to carry out the hydrolysis; carbon dioxide or hydrogen should serve equally well.

5. If it is found impossible to obtain a white product by crystallization, purification may be effected by dissolving the phloroglucinol dihydrate in four times its weight of hot boiling water and passing in sulfur dioxide until no further bleaching effect is observed (about half a minute is usually sufficient).

3. Methods of Preparation

Phloroglucinol is formed by alkaline fusion of many vegetable products, for instance, maclurin¹ or kino.² It is also formed to a small extent by the fusion of phenol with sodium hydroxide,³ and to a larger extent by fusing resorcinol with sodium hydroxide.⁴ It has been produced by fusing 1,3,5-benzenetrisulfonic acid with sodium hydroxide⁵ and 3,5-dibromophenol with potassium hydroxide.⁶ The best yields, however, are obtained by boiling a dilute solution of triaminobenzene hydrochloride⁷ or triamino-benzoic acid hydrochloride⁸ with water.

¹ Hlasiwetz and Pfaundler, *Ann.* **127**, 357 (1863); Benedikt, *Ann.* **185**, 114 (1877).

² Hlasiwetz, *Ann.* **134**, 122 (1865).

³ Barth and Schreder, *Ber.* **12**, 417 (1879).

⁴ Barth and Schreder, *Ber.* **12**, 503 (1879).

⁵ Barth and Schreder, *Ber.* **12**, 422 (1879).

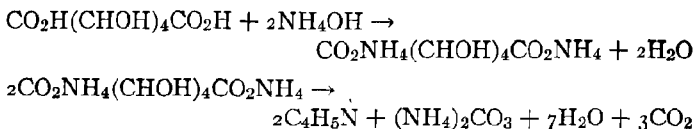
⁶ Blau, *Monatsh.* **7**, 632 (1886).

⁷ Weidel and Pollak, *Monatsh.* **21**, 20 (1900).

⁸ *Ger. Pat.*, 102358 [*Frđl. V.* 156 (1897)].

XXVII

PYRROLE



Submitted by S. M. McELVAIN and K. M. BOLLIGER.

Checked by H. T. CLARKE and E. R. TAYLOR.

1. Procedure

IN a 30-cm. evaporating dish or a Pyrex tray are placed 630 g. (3 moles) of mucic acid (Note 1) and 900 cc. of ammonium hydroxide (sp. gr. 0.9); this mixture is rapidly stirred to a smooth paste under the hood. The paste is evaporated to complete dryness on a steam bath, and the resulting ammonium mucate is powdered and mixed with 350 cc. of glycerol (Note 2) in a 5-l. round-bottom Pyrex flask. After standing overnight, the mixture is carefully distilled over a free flame, applying the heat to one side of the flask alone, so that only a portion of the mass is heated to the reaction temperature. The gases, which are evolved with considerable foaming (Note 3), are led away to a gas trap (Org. Syn. 8, 27) or to the open air, on account of their disagreeable nature. The heating is extended throughout the mass as rapidly as appears possible from the state of the mixture. Distillation is continued until a sample of distillate no longer shows oily drops when treated with solid potassium hydroxide; the total volume of distillate amounts to 900–1000 cc.

The entire distillate is redistilled until no further oil separates in the distillate; the watery layer is then separated and returned to the reaction flask, together with the water remaining in the distilling flask. Two liters more of water is added and about 800 cc. is distilled. The distillate is redistilled until 250–300 cc.

has collected in the receiver. This final distillate, on treatment with solid potash, yields a further 2 g. of oil.

The united oil is rapidly dried with a small quantity of solid potassium hydroxide (Note 4) and distilled. The fraction which boils at $127-131^{\circ}$ is collected; this is a colorless liquid which darkens on exposure to light (Note 5). The yield is 75-80 g. (37-40 per cent of the theoretical amount).

2. Notes

1. Mucic acid is now manufactured on a large scale by the oxidation of the galactose occurring in certain species of wood.

2. By the use of more glycerol the yield may be slightly increased, but the foaming is very difficult to control. Medicinal mineral oil may be substituted for the glycerol, but the yield is then considerably reduced.

3. Unless the flame is properly adjusted before the foaming becomes very pronounced, there may be difficulty in controlling the distillation. The best method consists in removing the flame from below the flask and allowing it to play on the upper portion of the vessel above the surface of the boiling mixture.

4. When pyrrole is allowed to stand over potassium hydroxide for more than a few hours, combination takes place, lowering the yield.

5. A product of rather better quality, which shows less tendency to darken, may be obtained by finally distilling under reduced pressure. The darkening may also be almost entirely avoided by storing the product in a sealed vessel.

3. Methods of Preparation

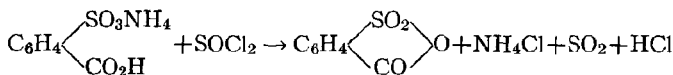
Pyrrole can be obtained by fractional distillation of bone oil and purification through the potassium derivative.¹ The only synthetic method offering any possibilities involves the thermal decomposition of ammonium mucate, either alone ² or in presence of glycerol.³

¹ Anderson, *Ann.* **105**, 349 (1858); Weidel and Ciamician, *Ber.* **13**, 65 (1880); Ciamician and Dennstedt, *Ber.* **19**, 173 (1886).

² Schwanert, *Ann.* **116**, 278 (1860).

³ Goldschmidt, *Zeit. f. Chem.* **1867**, 280; Khotinsky, *Ber.* **42**, 2506 (1909).

XXVIII

o-SULFOBENZOIC ANHYDRIDE

Submitted by H. T. CLARKE and E. E. DREGER.

Checked by HENRY GILMAN and J. E. KIRBY.

1. Procedure

In a 2-l. flask fitted with a mechanical stirrer, separatory funnel and an efficient reflux condenser are placed 219 g. (1 mole) of finely powdered acid ammonium *o*-sulfobenzoate (p. 1) and 200 cc. of dry benzene (Note 1). To this is added with stirring 145 g. (1.22 moles) of thionyl chloride (b. p. 76–78°). A tube is connected to the upper end of the reflux condenser which passes into an ice-cooled flask; from this another tube is provided to carry off the hydrogen chloride and sulfur dioxide generated during the reaction (Org. Syn. 8, 27). The mixture is gently warmed on a steam bath in such a way that gases are evolved fairly briskly (Note 2); continuous stirring is essential. The bulk of the entrained benzene and thionyl chloride is condensed in the ice-cooled receiver; the condensate is returned periodically to the reaction mixture through the separatory funnel. After about fifteen hours' heating, the evolution of gases slackens; an additional 400 cc. of dry benzene is then added and the heating continued until the evolution of gases ceases; this requires about five hours longer.

The hot mixture is then filtered (Note 3) with suction into a 2-l. flask and the solid material, consisting of ammonium chloride, is washed with 100 cc. of hot benzene. This solid is then returned to the 2-l. flask and boiled with stirring for one hour

with 300 cc. of dry benzene; the mixture while hot is then filtered with suction into the same 2-l. flask. The combined filtrates and washings are then distilled until about 300 cc. of benzene has been removed, after which the solution is cooled in an ice bath; this causes the greater part of the sulfobenzoic anhydride to crystallize. The benzene mother liquor is decanted from these crystals and the bulk of the solvent removed by distillation. The flask containing the crystals is attached to a condenser and heated until the solid has completely melted; the adhering solvent is then removed from the liquid by slightly reducing the pressure. The clear residue is poured into a dish and allowed to cool. The product thus obtained melts at 121–123°. The residue from the mother liquor, being as a rule somewhat dark in color, is preferably distilled under reduced pressure (Note 4), the flask being heated in a metal bath. The anhydride distils at 184–186°/18 mm. The second crop may have a slightly lower melting point. The total yield of *o*-sulfobenzoic anhydride, which is of sufficient purity for the preparation of sulfonphthaleins, amounts to 118–121 g. (64–66 per cent of the theoretical amount) (Note 5). In order to convert this into a product melting at 126–127° (Note 4), it is recrystallized from three times its weight of dry benzene.

2. Notes

1. The benzene is most satisfactorily dried by distillation, the moist forerun being rejected.
2. The reaction may become so vigorous that it is necessary to interrupt the heating for a short time.
3. The filtration should be carried out under a hood, on account of the presence of some unchanged thionyl chloride.
4. It is stated in the literature that the pure compound melts at 128°. It is very sensitive to moist air, which converts it into the free acid.
5. With larger quantities the yields are significantly increased; the submitters of these directions obtained 74–81 per cent of the theoretical amount with runs of 7.5 moles.

3. Methods of Preparation

o-Sulfobenzoic anhydride has been prepared from the free acid by heating alone or with phosphorus pentoxide¹ and by treating it with acetyl chloride;² from the neutral potassium salt by warming with phosphorus pentachloride;² from the acid potassium salt by warming with phosphorus pentachloride³ or thionyl chloride,⁴ and by heating it with phosphorus pentoxide to 400°. ⁵ The present method is a modification of that of White and Acree ⁶ who heated the acid ammonium salt with an excess of thionyl chloride and extracted the product with benzene.

¹ Remsen and Dohme, Amer. Chem. J. **11**, 343 (1889).

² Fahlberg and Barge, Ber. **22**, 757 (1889).

³ Schon, Amer. Chem. J. **20**, 258 (1898).

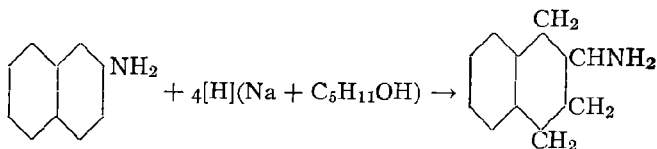
⁴ Cobb, Am. Chem. J. **35**, 499 (1906).

⁵ Heitman, J. Am. Chem. Soc. **34**, 1594 (1912).

⁶ White and Acree, Am. Chem. J. **41**, 1197 (1919).

XXIX

αα-TETRAHYDRO- β -NAPHTHYLAMINE



Submitted by E. B. H. WASER and H. MÖLLERING.

Checked by ROGER ADAMS and W. W. MOYER.

1. Procedure

A 1-l. wide-neck round-bottom flask is set into an iron dish of about 1.3-1.5 l. capacity and the space in between is filled with fine sand so that the flask rests about 1 cm. from the bottom of the dish (Note 1). In the flask is placed 26 g. (1.1 moles) (twice the theoretical amount) of sodium cut into thin slices (Note 2), and the flask is then closed with a tight-fitting cork stopper through which is inserted a separatory funnel (Note 3) and a long, wide, Liebig condenser through the jacket of which is passed downward a rapid current of air (Note 4).

While preparing this set-up a solution of 20 g. (0.14 mole) of β -naphthylamine in 250 cc. of isoamyl alcohol (dried by distilling off a moist forerun) is heated to boiling. The boiling solution is poured in a stream through the separatory funnel into the flask upon the sodium and then washed down with 50 cc. of boiling isoamyl alcohol. A very violent reaction begins immediately which slows up after about five minutes and then must be aided by warming. The flame is so regulated that the reaction mixture is always boiling very vigorously until all of the sodium is dissolved. This generally requires about three

or four hours. If after three hours the sodium is not completely dissolved it is advisable, in order to hasten the reaction, to add 50 cc. more of isoamyl alcohol.

When all of the sodium is completely dissolved, the hot, yellow solution is allowed to cool to about 100° and then poured into 500 cc. of cold water. The mixture is allowed to cool completely with frequent shaking and then the upper isoamyl alcohol layer is separated from the water layer which contains the principal part of the sodium hydroxide.

The reduction is repeated four times with 20 g. of β -naphthylamine so that altogether 100 g. of naphthylamine has been reduced (Note 5). The isoamyl alcohol solutions from all five portions are combined and concentrated hydrochloric acid is added until the solution is just acid to litmus. For this purpose usually about 40–50 cc. is needed (Note 6). The greater part of the isoamyl alcohol is now distilled from a large flask (about 900–1100 cc. is recovered). The distillation is continued until a crust of crystals starts to form, and the residue is then cooled and treated with 200–300 cc. of water and about 300 cc. of 50 per cent potassium hydroxide solution. The base which separates is extracted in the separatory funnel with four 400–500 cc. portions of ether and the ether extracts combined in a flask with a wide neck.

The flask is set in ice water and a rapid stream of carbon dioxide which has previously passed through two wash bottles containing water (Note 7), is passed in. After about a quarter of an hour the liquid begins to become cloudy and soon after there follows a rather rapid separation of the carbonate of the strongly basic alicyclic compound, while the aromatic base does not react and remains in solution. The carbon dioxide is passed in continuously until no more carbonate separates; this requires about four to six hours. The carbonate is filtered by suction on a Büchner funnel and washed with a little dry ether. The filtrate is again treated with carbon dioxide; there is often obtained still more carbonate which is added to the precipitate (Note 8).

For further purification, the almost dry carbonate is dissolved

in 500–600 cc. of 7 per cent acetic acid and the solution is filtered from the dark impurities. The clear, almost colorless solution is decomposed with a large excess of potassium hydroxide (about 200 cc. of a 50 per cent solution), whereupon the alicyclic base separates as a light-brown oil which collects on the surface of the water solution and is extracted as rapidly as possible by shaking three or four times with ether. The ether solution is dried for

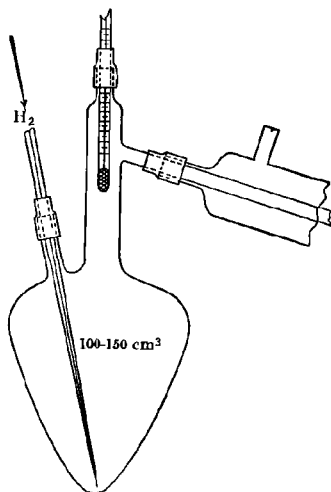


FIG. 1.

at least six hours with about 90–100 g. of potassium hydroxide (Note 9). The distillation of the ether is carried out most conveniently in a specially designed Claisen flask (Org. Syn. 1, 40) of a 100–150 cc. capacity, the ether solution gradually being added to the flask from the separatory funnel.

The base is distilled in a vacuum obtained by a water pump, because it is easily decomposed under ordinary pressure. For this distillation a flask of the form shown in Fig. 1 is recommended for use (Note 10) though not essential.

Since the base is sensitive to oxygen, dry hydrogen is passed through the capillary tube used in the distillation (Note 11). The distillation of the base runs very smoothly and the liquid

distils over from beginning to end almost constantly within a degree.

The yield of pure distilled base, b.p. 118.5°/8 mm., 127.5–128°/12 mm., 140–140.5°/20 mm., amounts to 53–59 g. (51–57 per cent of the theoretical amount). The pure base can be preserved only by sealing it in ampules (containing as little air as possible) immediately after distillation. The *ac*-tetrahydro- β -naphthylamine is a colorless, water-clear liquid which shows no fluorescence (Note 12), and possesses a strong odor similar to piperidine. In the air the base soon turns brown, rapidly absorbs carbon dioxide and changes to the carbonate.

The hydrochloride of the *ac*-tetrahydro- β -naphthylamine can be obtained readily by neutralizing a dry ether solution of the base with an ether solution of hydrogen chloride. It crystallizes from water in large plates which melt at 237°.

2. Notes

1. In place of the sand bath it is possible to use an ordinary wire gauze or a Babo's air bath but the danger of a fire due to a sudden breaking of the flask during the very violent reaction at the beginning is considerably greater. The experiment is best carried out using a sand bath. The hands should be protected with gloves and the eyes with glasses.

2. After many experiments this amount of sodium was found to be the optimum. By the use of smaller quantities of sodium and β -naphthylamine the yield drops; with larger amounts the danger of breaking the glass flask increases. It is probably possible to use copper flasks but it is then impossible to see how the reaction is running.

3. The stopcock of the separatory funnel must have as wide a hole as possible so that the isoamyl alcohol can enter in a rapid stream.

4. If a water condenser is used the condensation is much more efficient but the danger of breaking is then much greater. A brass inner tube in place of a glass one is desirable. If the condenser tube is too narrow, there is danger that the violently

boiling isoamyl alcohol will be thrown out at the beginning of the reaction because it cannot flow back.

5. By working up less than 100 g. of β -naphthylamine the yield decreases rather rapidly on account of the various possibilities for loss in the later operations.

6. An excess of acid does no harm but makes the recovery of the isoamyl alcohol more difficult.

7. If an efficient reflux condenser is attached to the flask the major part of the ether can be recovered. It is necessary to be sure that the carbon dioxide is actually moist because otherwise the carbonate will not form at all or only very slowly.

8. The ether filtrates contain dihydronaphthalene and *ac*-tetrahydro- β -naphthylamine.

9. Since the free base reacts very strongly alkaline and also is sensitive, it is not possible to allow it to remain long in the air or loss will occur due to carbonate formation and oxidation.

10. The suggested flask has the following advantages over other forms:

(a) The chance for contaminating the boiling base with rubber is reduced to a minimum; the capillary and thermometer are attached to the distillation flask by means of small rubber tubing.

(b) The loss due to the substance which remains on the walls of the flask is reduced to a minimum as compared to other flasks.

(c) The substances can, with the help of the capillary be distilled over to the last drop, which is not possible in a round flask.

11. This apparatus has also proved itself very useful for the distillation of other substances sensitive to oxygen.

12. Fluorescence arises from aromatic by-products which, however, can be entirely separated by careful work. Pure *ac*-tetrahydro- β -naphthylamine gives no color with diazobenzene sulfonic acid.

13. Of special interest is the extremely powerful physiological action of the tetrahydro base and its salts,¹ which makes

¹ Bamberger and Filehne, Ber. 22, 777 (1889); Stern, Virchows Archiv., 115, 14 (1889); 117, 418 (1889); Pick, Arch. f. exp. Pathologie u. Pharmakologie

it advisable to handle it carefully. The action can be called a symptom-complex to which Barger has assigned the name, "sympathomimetic," and it consists in a maximum dilation of the pupils (mydriasis), in a marked increase in the arterial blood pressure and in an increase in the rapidity of breathing.

3. Methods of Preparation

Up to the present the only method used for the reduction of β -naphthylamine for obtaining the tetrahydro base has been with sodium and alcohol. This method was first described by Bamberger and Müller.² It is possible to substitute ethyl alcohol for amyl alcohol but the yield is distinctly lower. The base has been resolved into its optically active components.³

(A. Path.) **42**, 399 (1899); Weichowsk, A. Path. **52**, 417 (1905); Jonescu, A. Path. **60**, 345 (1909); Cloetta and Waser, A. Path. **73**, 398, 436 (1913), **75**, 406 (1914); **77**, 16 (1914); **79**, 30 (1915); **98**, 198 (1923); Sacharof, Zeitschr. f. exp. Pathologie u. Therapie, **7**, 225 (1909).

² Bamberger and Muller, Ber. **21**, 847 (1888); see also Bamberger and Kitschelt, Ber. **23**, 876 (1890); Waser, Ber. **49**, 1202 (1916); Cloetta and Waser, A. Path. **73**, 398 (1913); **98**, 198 (1923).

³ Pope and Harvey, J. Chem. Soc. **79**, 74 (1901), Waser, A. Path. **73**, 401 (1913).

LATER REFERENCES TO PREPARATIONS IN PRECEDING VOLUMES

(The following references are to methods of possible preparative value that have been recently described. The numbers in parentheses following the name of a compound refer to the volume and page of Organic Syntheses.)

Acetal (3, 1):

(a) From ethyl alcohol and paraldehyde, using *p*-toluenesulfonic acid or hydrogen chloride as catalyst. BEDUWÉ, Bull. soc. chim. Belg. **34**, 41 (1925).

(b) By the interaction of ethyl alcohol and metaldehyde in presence of calcium chloride, a trace of hydrogen chloride, and high-boiling (200–300°) petroleum. The acetal is removed from the reaction mixture by virtue of its solubility in the petroleum. The yields are stated to reach 90 per cent of the theoretical amount. FOUQUE and CABANAC, Bull. soc. chim. **39**, 1184 (1926).

(c) Calcium chloride is stated to be a better catalyst than ferric chloride for the formation of diethyl acetal, though the reverse is the case for dimethyl acetal. ADAMS and ADKINS, J. Amer. Chem. Soc. **47**, 1358 (1925).

Acetamide (3, 3):

By passing the vapor of methyl alcohol and hydrogen cyanide over catalysts at high temperatures. SMITH and SMITH, can. pat. 274,065 (1927).

Adipic acid (5, 9):

Isolation from cellulose waste liquors. MELANDER and WALLIN, Swed. pat. 62,919 [C. A. **21**, 4069(1927)].

***l*-Arabinose (8, 18):**

Same procedure as described in Org. Syn. ANDERSON and SANDS, J. Am. Chem. Soc. **48**, 3172 (1926).

Butyl Butyrate (5, 23):

By oxidizing butyl alcohol with sodium chlorate and dilute sulfuric acid, using vanadium pentoxide as a catalyst. MILAS, J. Amer. Chem. Soc. 50, 493 (1928).

This reaction may lead to violent explosions if the sodium chlorate be replaced by potassium perchlorate and if the temperature be not carefully controlled. WAGNER, J. Amer. Chem. Soc. 50, 1233 (1928).

***p*-Cresol (3, 37):**

Traces of isomeric cresols may be removed by treatment with quinone chloroimide. GIBBS, J. Amer. Chem. Soc. 49, 839 (1927).

Cyclopentanone (5, 37):

Occurrence in lignite distillation products. VORLÄNDER and GÖRNANDT, Z. Angew Chem. 39, 1116 (1926).

Ethyl cyanoacetate (3, 53; 8, 74):

The W. A. NOYES method of preparation [J. Am. Chem. Soc. 26, 1545 (1904)] from ethyl chloroacetate and potassium cyanide in methyl alcoholic solution gives a mixture of methyl and ethyl esters. URUSHIBANA, Bull. Chem. Soc. Japan 2, 143 (1927) [C. A. 21, 2879 (1927)].

2-Furancarboxylic acid (6, 44):

Subsequent to the Cannizzaro reaction, sufficient sulfuric acid is added to liberate substantially all of the pyromucic acid and to cause resinification *in situ* of the 2-furycarbinol when the mixture is heated. TRICKEY and MINER, U. S. pat. 1,665,236 [C. A. 22, 1783 (1928)].

Furfural (1, 49):

From oat hulls. BRONLEE, Ind. Eng. Chem. 18, 422 (1927).

***d*-Glutamic acid (5, 63):**

Recovery from molasses waste. TRESSLER, Can. pat. 268,728. [C. A. 21, 2395 (1927).]

Glycerol α -monochlorhydrin (2, 33):

By heating epichlorhydrin with water in the presence of sulfuric acid as a catalyst. FOURNEAU and RIBAS Y MARQUÈS, Bull. soc. chim. (4) 39, 700 (1926); see also BOESEKEN and HERMANS, Rec. trav. chim. 42, 1106 (1923).

Hydroxylamine salts (3, 61):

By electrolytic reduction of sodium nitrate in 65 per cent sulfuric acid. PONZIO and PICHETTO, Chem. Abstr. 19, 239 (1925).

Mandelic acid (6, 58):

From phenylglyoxal by means of biocatalysts. [MAYER, Biochem. Z. 174, 420 (1926)] and by enzyme action [KUHN and HECKSCHER, Z. physiol. Chem. 160, 116 (1926)].

Mercury Di-*p*-Tolyl (3, 65):

By treating *p*-tolyl mercuric chloride with copper in pyridine. This appears to be a general method. HEIN and WAGLER, Ber. 58, 1499 (1925).

***m*-Nitro Chlorobenzene (3, 79):**

From *m*-nitroaniline by the Sandmeyer reaction. KOHMAN, J. Phys. Chem. 29, 1052 (1925).

Nitromethane (3, 83):

By heating methyl *p*-toluenesulfonate with sodium nitrite. RODIONOW, ALEXEIEFF and CARCARRAS, Bull. Soc. Chim. (4) 39, 324 (1926).

***m*-Nitrophenol (3, 87):**

Formed in 2-3 per cent yield (together with ortho and para derivatives) by nitrating phenol in glacial acetic acid. ARNALL, J. Chem. Soc. 125, 811 (1924).

Nitrourea (5, 85):

New method of purification by recrystallization from alcohol. WILLSTÄTTER and PFANNENSTIEL, Ber. 59B, 1870 (1926).

Quinizarin (6, 78):

Differs from the general procedure described in Org. Syn. by starting with a mixture of *o*- and *p*-chlorophenol and heating above 200°. DODD, SPRENT and United Alkali Co., Ltd., Brit. pat. 245,584 (1924). [C. A. 21, 249 (1927)].

Styrene (8, 84):

Separated from carburetted water gas drip oil by fractionation. BROWN, U. S. pat. 1,640,975 [C. A. 21, 3449 (1927)].

SUBJECT INDEX

(This Index Comprises Material from all Volumes of this Series)

(Names of compounds in small capital letters indicate substances for which directions are given, the numbers in bold face type refer to volumes of Organic Syntheses, numbers in italics refer to pages in those volumes on which preparative directions are given, and numbers in Arabic refer to pages on which the compounds or subjects are mentioned in connection with other preparations. For example: ACETOACETIC ESTER, **4**, 45; **6**, 36 indicates that acetoacetic ester is mentioned in volume 4 on page 45 and that directions for its preparation are given in detail in volume 6 on page 36; Acetophenone, **2**, 1 indicates that this substance is mentioned in volume 2 on page 1 but that no directions for its preparation are given in this series.)

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